Cache Valley Air Quality Studies

A Summary of Research Conducted
(through 2006)

prepared by
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EXECUTIVE SUMMARY

The Cache Valley airshed is in serious threat of exceeding the U.S. National Ambient Air Quality Standard (NAAQS) for Particulate Matter less than 2.5 μm in diameter ($PM_{2.5}$). Although the local airshed approaches both the annual (15 μg m^{-3}) and the 24-hr standard (65 μg m^{-3}), it is the 24-hr standard that is in the greatest danger of exceedance. As of June 2006, the regulatory allowable 98th percentile value for 2006, roughly the eighth highest value) can only be 33.2 μg m^{-3} without exceeding the NAAQS. To date, this value has been exceeded four times. For comparison, the target value was exceeded 6, 41, and 39 times in the years 2003, 2004, and 2005, respectively. It should also be noted that the U.S. EPA is currently considering lowering the 24-hr standard to 35 μg m^{-3}.

The Cache Valley $PM_{2.5}$ is somewhat uniquely a wintertime problem, when low lying, persistent radiation and subsidence inversions set up, trapping pollutants in the Valley for extended periods of time, allowing photochemically-derived particulate material to become elevated. Chemical analysis by researchers at Utah's Division of Air Quality and Air Monitoring Center, as well as Utah State University, have shown that 50-95% of the $PM_{2.5}$ collected at the Logan site is composed of ammonium nitrate (NH_4NO_3).

In order to understand the local pollutant behavior and identify the most appropriate remediation scenarios, several sequential and parallel research programs have been conducted by Dr. Randy Martin and others at Utah State University. This document summarizes these efforts and attempts to coalesce these studies into a single report.

1) PM Homogeneity
   - Statistically (95% CI), the Cache Valley is homogeneous with regard to $PM_{2.5}$ concentrations during inversion episodes, although some site-to-site variation may exist. The areas which trended lower in concentrations were the extreme southeast (Hyrum) and west (Mendon) portions of the Valley. As a partial result of these studies, FRM regulated monitoring stations were established in Hyrum, UT, Amalga, UT, Prestion, ID, and Franklin, ID.

2) Valley Ambient Ammonia
   - Based on measurements at the Logan location, the Valley's wintertime formation of ammonium nitrate was found to be limited by the availability of nitrate, specifically nitric acid (HNO_3). The ambient Logan wintertime NH_3 averaged (24-hr) 9.2 μg/m^3 (13.9 ppb). Furthermore, following these data, the Cache Valley was found to be NH_3-rich by a factor of approximately two. Comparisons of wintertime ambient NH_3 concentrations between the Valley's urban area (Logan) and a rural location (Amalga), showed the rural area averaged ≈2.5 times the NH_3 of the urban site.

3) On-road Automobile Emissions
   - The study found that approximately 4.5% and 10.3% of the Valley's vehicles would fail inspections tests for NO_x and VOCs, respectively, and that these vehicles were responsible for 25.4% and 47.8% of the valley-wide emissions. The study also found

that the majority of the vehicles that would fail would be older than 1996. As of 2004, vehicle registrations from the Utah Department of Motor Vehicles showed the percentage of vehicles that are 1996 or newer be 49.4%, and, therefore, eligible for I & M testing with the simpler on-board diagnostic (OBD) method.

4) Public & Student Phone Survey
   -

5) Inversion Heights (dT/dz)

6) Indoor/Outdoor $PM_{2.5}$ Concentrationss

7) Wintertime Vertical Ozone Profile

8) VOCs

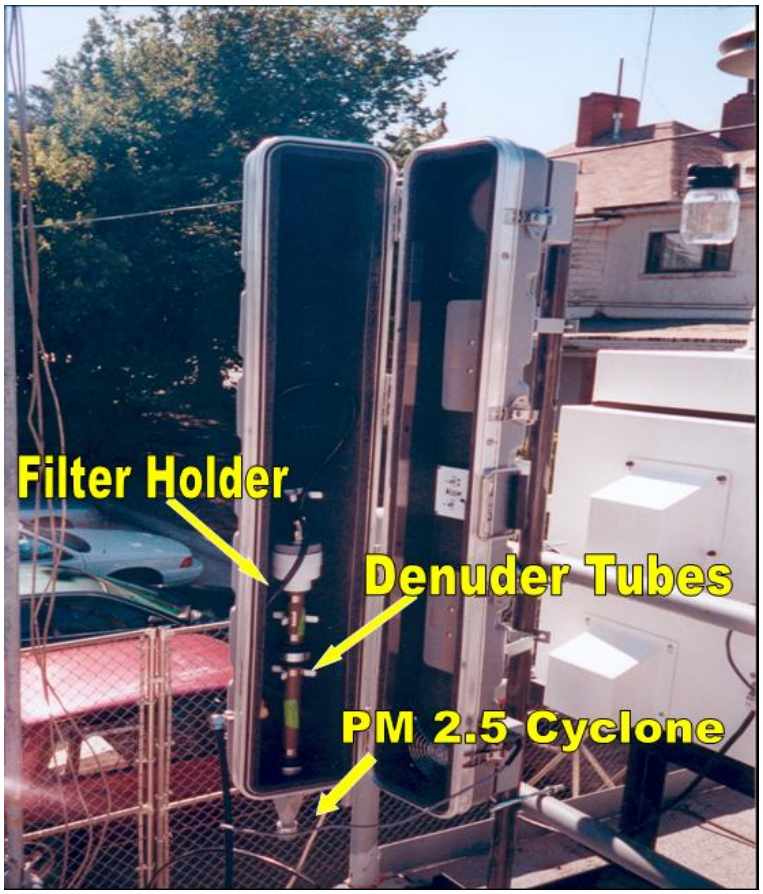
Cache Valley on a "good" day (Feb. 25, 2002)

Cache Valley on a "moderate" day (Feb. 23, 2002: $PM_{2.5} \approx 40\ \mu g/m^3$)

Cache Valley on a "very bad" day (Feb. 16, 2004; $PM_{2.5} = 101.6\ \mu g/m^3$), viewed from adjacent 6300 ft asl ridge top

Installing a portable AirMetrics' MiniVol $PM_{2.5}$ sampler

Recovering a temperature sensor form the ridge above Logan



URG ammonia and acid gas denuder system installed at the Logan site.

Passive ammonia samplers (with and without rain cap)

Cache Valley on-road vehicle exhaust measuremnt

On-road “Red Day’ notification signage Main Street in Logan

MiniVol samplers during indoor vs. outdoor studies

Teflon nozzle and tubing during ozone vertical profile flight (Feb. 9, 2006: 14:57) -- also note visible inversion layer

ACKNOWLEDGMENTS

The investigators would like to thank the State of Utah and Utah State University for partial funding under the Community/University Research Initiative (CURI) Grant program. Utah's Department of Environmental Quality's Division of Air Quality (DAQ) and Air Monitoring Center (AMC) are also to be gratefully thanked for funding several different aspects of the studies described within this document. Additional funding for personnel and supplies was obtained through the Utah Water Research Laboratory (UWRL).

The authors would also like to thank Bob Dalley, Neal Olson, Dave McNeill, Brock LaBaron, Tyler Cruckshank, Bruce Allen, Ran McDonald, Joe Thomas, Cheryl Heying, and Rick Sprott for their cooperation in supplying equipment, comparative data, and expertise. Personnel from the Bear River Health Department were also instrumental in the research described herein and are also owed a great deal of thanks and appreciation. Additional acknowledgements go to USU students Thomas Bradley, Hosam Jamal, and Demetrio Cabanillas for their participation in various aspects of this project.

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OVERALL INTRODUCTION

The elevated wintertime levels of $PM_{2.5}$ in Utah's Cache Valley have been the subject of concern since measurements of the criteria pollutant began in the spring of 2000. As shown in Table 1, the airshed has flirted with exceeding National Ambient Air Quality Standard, especially the 24-hr value (65 $\mu g\ m^{-3}$), since the first complete 3-yr data set was obtained.

Table 1. Regulatory $PM_{2.5}$ values for Logan, UT (UDAQ, 2006).

Year	Annual Average	24-hr 98th Percentile
2001	15.6 $\mu g\ m^{-3}$	71.1 $\mu g\ m^{-3}$
2002	14.7 $\mu g\ m^{-3}$	58.4 $\mu g\ m^{-3}$
2003	8.4 $\mu g\ m^{-3}$	31.5 $\mu g\ m^{-3}$
3-yr Avg	**13.0 $\mu g\ m^{-3}$**	**54.8 $\mu g\ m^{-3}$**
2004	15.3 $\mu g\ m^{-3}$	101.5 $\mu g\ m^{-3}$
3-yr Avg	**12.8 $\mu g\ m^{-3}$**	**63.8 $\mu g\ m^{-3}$**
2005	13.0 $\mu g\ m^{-3}$	61.7 $\mu g\ m^{-3}$
3-yr Avg	**12.1 $\mu g\ m^{-3}$**	**64.9 $\mu g\ m^{-3}$**
2006 Allowable	----	33.2 $\mu g\ m^{-3}$

Compositional research conducted by Utah's Division of Air Quality (DAQ) and Air Monitoring Center (AMC), as well as investigators at Utah State University, showed that the bulk of the fine particulate material consisted of ammonium nitrate (NH_4NO_3) (UDAQ, 2006). During "typical" winter days, it was shown that average NH_4NO_3 content accounted for 50-60% of the particulate material, on elevated days (> 65 $\mu g\ m^{-3}$), the NH_4NO_3 fraction approached 80-95%.

The discovery of the elevated levels of $PM_{2.5}$ in the Cache Valley motivated several research studies to identify the dominant causes and potential areas of remediation. These efforts are described within this document. Specifically, this report summarizes research into Cache Valley's PM_{10} and $PM_{2.5}$ homogeneity, determination of ambient levels of gas-phase ammonia (NH_3) and it's role in limiting particulate formation, local on-road vehicle emissions, local attitudes toward potential particulate control scenarios, inversion heights, indoor vs. outdoor $PM_{2.5}$ concentrations, research into ambient (rural and urban) concentrations of volatile organic compounds (VOCs), and continuing research of vertical ozone profiles and indoor ammonia.

It should be noted that these research programs include funding through Utah's DAQ and AMC, but also other sources including Utah State University, The Utah Water Research Laboratory, and the Bear River Health Department.

VALLEY-WIDE PM_{10} AND $PM_{2.5}$ SATURATION (HOMOGENEITY) STUDIES

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INTRODUCTION

Among the first projects studied in cooperation with the Utah's Division of Air Quality and Utah State Universities Air Quality Research Group within the Department of Civil and Environmental Engineering (CEE) and the Utah Water Research Laboratory (UWRL) was the examination of the potential homogeneity of PM_{10}, and then $PM_{2.5}$, throughout the Cache Valley. The impetus for this study began in the fall of 2001 with comparisons of ambient PM_{10} and $PM_{2.5}$ as measured at the Smithfield, UT residence of Dr. Randy Martin and those monitored by the DAQ at the Logan city sampling location (approximately 11 kilometers apart). Figures 1 and 2 show the 2002 comparisons for PM_{10} and $PM_{2.5}$, respectively.

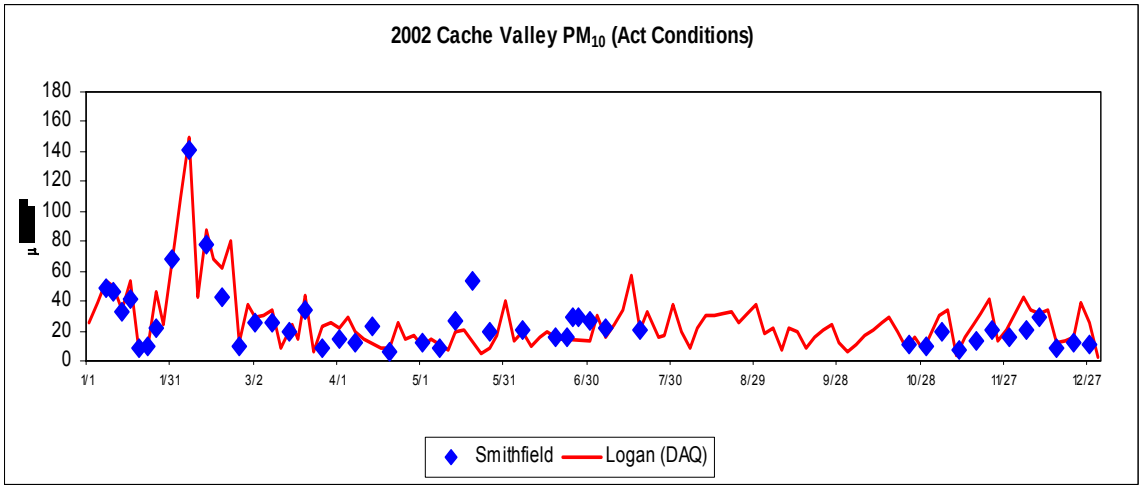

Figure 1. Comparison of Logan and Smithfield 2002 ambient PM_{10} concentrations.

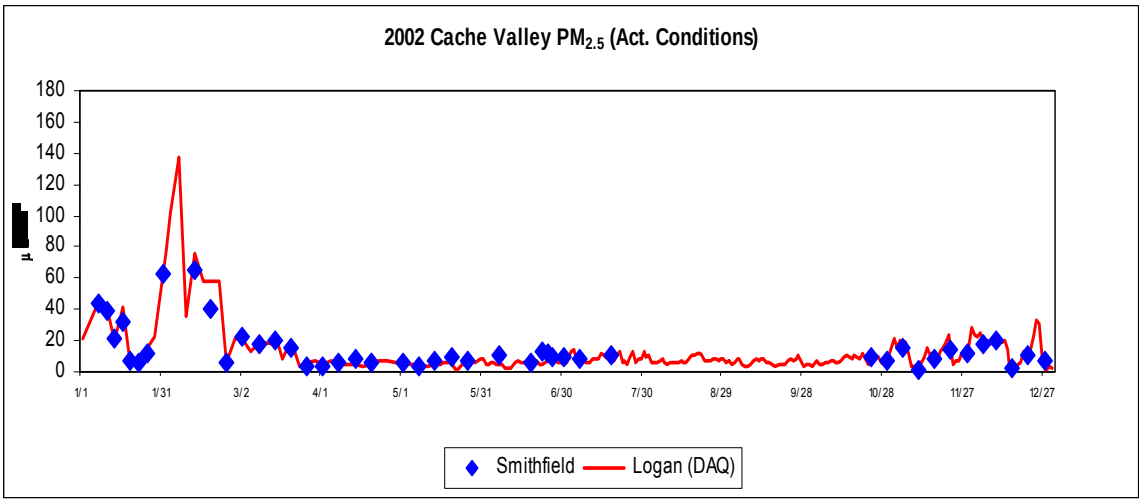

Figure 2. Comparison of Logan and Smithfield 2002 ambient $PM_{2.5}$ concentrations.

As is shown above, the concentrations trends and absolute values are very similar for both sites, including the elevated levels recorded during the wintertime inversion episodes. When similar data for the 2003 calendar year are included, the correlation (R^2) between the two sites was 0.819 and 0.923 for PM_{10} and $PM_{2.5}$, respectively. Although not statistically quantifiable, visual examination of the plotted data, for both size fractionations, seem to show a slight positive (greater than) difference at the Smithfield location in the summer and a slight negative (less than) difference in the winter. This could be a reflection of the somewhat more rural nature of the Smithfield location.

Cache Valley's high, "official" wintertime $PM_{2.5}$ concentrations, as measured at the single Logan city sampling site, the similar PM_{10} and $PM_{2.5}$ trends observed at the separate Smithfield location, the abundance of secondary material, and visual observations suggested that the particulate pollution was likely not an isolated problem centered around the Logan location, but more likely homogeneous throughout the Cache Valley. In order to investigate this hypothesis, five portable PM_{10} samplers were deployed throughout the Valley and operated during the winter of 2002/2003. These samplers were further compared to the DAQ operated Logan location and a paired set of federal reference method (FRM) PM_{10} and $PM_{2.5}$ samplers deployed at the Smithfield site.

As will be further discussed in following sections, the preliminary study conducted in during the winter of 2002/2003, at the (equipment) limited number of available sites, showed that the Valley's PM_{10} was statistically homogeneous across the compared locations. Although the data did suggest overall ambient particle homogeneity, the unexpectedly low particulate concentrations during the examined winter (refer back to Table 1), the variability in the relationship between PM_{10} and $PM_{2.5}$, and the limited number of available samplers left it uncertain as to whether the airshed was truly homogeneous with respect to $PM_{2.5}$, particularly at levels above the NAAQS. In order to more fully investigate this question, fifteen portable $PM_{2.5}$ samplers were deployed throughout the Cache Valley and operated during the winter of 2003/2004. Also as before, two federal reference method (FRM) $PM_{2.5}$ samplers were also deployed, including the Logan UDAQ regulatory and the Smithfield $PM_{2.5}$ sampling sites.

METHODOLOGY

2002/2003 PM_{10} Homogeneity (Saturation) Study

In an attempt to bracket typical wintertime conditions, the initial PM_{10} homogeneity study took place from October 24, 2002 through February 26, 2003, with a nominal sampling frequency of every six days. The samples were targeted to run for 24 hours, midnight to midnight, on each of the sample days. In addition to the Logan city sampling site (UTM 430309 E, 4619926 N, zone 12), six additional sites were established throughout Utah's Cache Valley. These sites were located 2.9 km ENE (USU Campus), 3.9 km S (Evan's Farm/Nibley), 5.5 WNW (Cache Valley Hunter Education Center), 9.5

km SSW (American Heritage West Center), 10.9 km N (Smithfield), and 17.1 km NW (Newton) of the Logan sampling location.

Five portable AirMetrics PM_{10} MiniVol samplers (Airmetrics, 2004) were borrowed from the Division of Air Quality of Utah's Department of Environmental Quality (DEQ). These instruments were deployed at all but the Smithfield location. At the time of the described study, equivalent $PM_{2.5}$ samplers were not available to the investigators. The MiniVol Samplers operate via a battery-powered pump, which draws air through an impactor specifically-designed to separate the larger particle fraction (>10 μm), allowing the PM_{10} material to be collected on a subsequent 47 mm Teflon filter. The filters were equilibrated at room temperature, in an air-tight desiccator, and weighed on a 5-place (gram-based) balance pre- and post-exposure until triplicate weights within 0.05 mg were obtained.

The samplers are designed to operate at an actual flowrate of 5 Lpm, with flow controlled via a manually set rotameter. Prior to sampling, each system was calibrated using a soap-bubble meter and a calibration equation was developed relating local temperature and pressure and the rotameter reading to the flowrate at actual conditions. For a given sampling run, the expected average temperature and pressure were estimated, the necessary rotameter setting for the required 5 Lpm (actual) was determined, and the flow was adjusted so that when the system's internal alarm initiated the sampling period, the proper flowrate would be obtained. An on-board elapsed time counter registered the actual duration of any given sampling period (some runs were abbreviated due to battery failure), which when combined with the rotameter flowrate, was used to determine the sample volume.

At the Smithfield location, a paired set of $PM_{2.5}/PM_{10}$ FRM Samplers (Andersen Instruments, RAAS 2.5-100) were operated by the investigators following the basic regulatory guidelines outlined in 40 CFR 50, Appendix L (40CFR50, 2003). The FRM samplers at the Logan site, the DEQ's official Cache Valley sampling location, were operated by DAQ and Bear River Health Department (BRHD) personnel, who shared the collected data with the project investigators.

Furthermore, the comparability, and the necessity of any potential correction factors, of the portable MiniVol samplers to the FRM samplers was examined via separate co-located sampling runs, in addition to the scheduled sampling periods. For this co-located investigation, the MiniVols were placed next to the Smithfield FRM samplers and each was operated as normal for four separate, 24-hour sampling periods.

2003/2004 $PM_{2.5}$ Homogeneity (Saturation) Study

As before, since Cache Valley's $PM_{2.5}$ problem is generally limited to winter periods, the next phase of the particle saturation study took place from November 11, 2003 through February 27, 2004, with a nominal sampling frequency of every six days. A significant inversion, and accompanying $PM_{2.5}$ episode, took place January 7-24, 2005 and during this period, the samplers were operated every other day. The samples were

targeted to run for 24 hours, midnight to midnight, on each of the sample days. In addition to the Logan city sampling site (UTM 430309 E, 4619926 N, zone 12), sixteen additional sites were established throughout the Cache Valley. The additional sites were located in or near surrounding Utah communities of Wellsville, Hyrum, USU's Animal Science Farm (ASF), USU's Evan's Farm, Mendon, Cache Valley Hunter Education Center (Hunter Ed), the Utah State University campus (USU), Ballard Junction, Smithfield, Amalga, Newton, Clarkston, Richmond, and Cornish. Two sites were also established on the Idaho side of the Cache Valley, at the towns of Franklin and Preston. Figure 3 shows the various sites' location in terms of UTM (NAD27) coordinates.

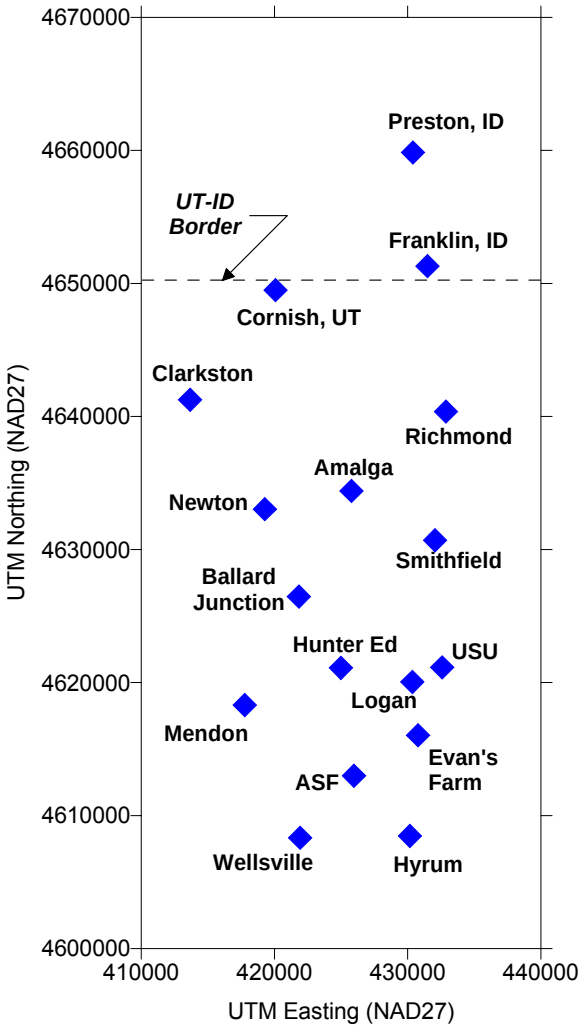

Figure 3. Relative Cache Valley sampling locations for the 20003-2004 $PM_{2.5}$ saturation study.

The fifteen portable AirMetrics $PM_{10/2.5}$ MiniVol samplers (AirMetrics, 2004) were obtained from the Air monitoring Center (AMC) of Utah's Department of Environmental Quality (DEQ). These instruments were deployed at all but the Smithfield location. The MiniVol samplers operate via a battery-powered pump, which draws air through an impactor specifically-designed to separate the larger particle

fraction (>2.5 μm), allowing the PM_{10} or $PM_{2.5}$ (depending on the sample head) material to be collected on a subsequent 47 mm Teflon filter. The filters were equilibrated at room temperature, in an air-tight desiccator, and weighed on a 6-place (gram-based) microbalance pre- and post-exposure until triplicate weights within 0.005 mg were obtained.

The samplers are designed to operate at an actual flowrate of 5 Lpm, with flow controlled via a manually set rotameter. Prior to testing, each system was calibrated using a soap-bubble meter and a calibration equation was developed relating local temperature and pressure and the rotameter reading to the flowrate at actual conditions. For a given sampling run, the expected average temperature and pressure were estimated, the necessary rotameter setting for the required 5 Lpm (actual) was determined, and the flow was adjusted so that when the system's internal alarm initiated the sampling period, the proper flowrate would be obtained. An on-board elapsed time counter registered the actual duration of any given sampling period (some runs were abbreviated due to battery or pump failure, programming errors, etc.) which, when combined with the calibrated rotameter flowrate, was used to determine the sample volume.

At the Smithfield location, a $PM_{2.5}$ FRM sampler (Andersen Instruments, RAAS 2.5-100) was operated by the investigators following the basic regulatory guidelines outlined in 40 CFR 50, Appendix L (40CFR50, 2003). The $PM_{2.5}$ FRM (Rupprecht and Patashnick) sampler at the Logan site, the DEQ's official Cache Valley sampling location, was operated by DAQ and BRHD personnel, who shared the collected data with the project investigators.

Once again, the comparability, and the necessity of any potential correction factors, of the portable MiniVol samplers to the FRM samplers was examined through four separate co-located test runs. For the co-located investigations, the MiniVols were placed adjacent to and at the same elevation as the Logan FRM sampler and operated to concurrent time periods.

RESULTS AND DISCUSSION

2002/2003 PM_{10} Homogeneity (Saturation) Study

Co-location of the MiniVol samplers with the Andersen FRM PM_{10} sampler showed the portable samplers consistently reported higher PM_{10} concentrations for all of five of the individual instruments. The overall average error was found to be +27%. As can be seen in Figure 4, the tested MiniVols over predicted the PM_{10} concentrations by approximately 15-40%. Given the magnitude of these percentages and the relative tightness of their individual confidence intervals, the final data analysis calculations for the describe saturation study included the appropriate individual instrumentation correction factors.

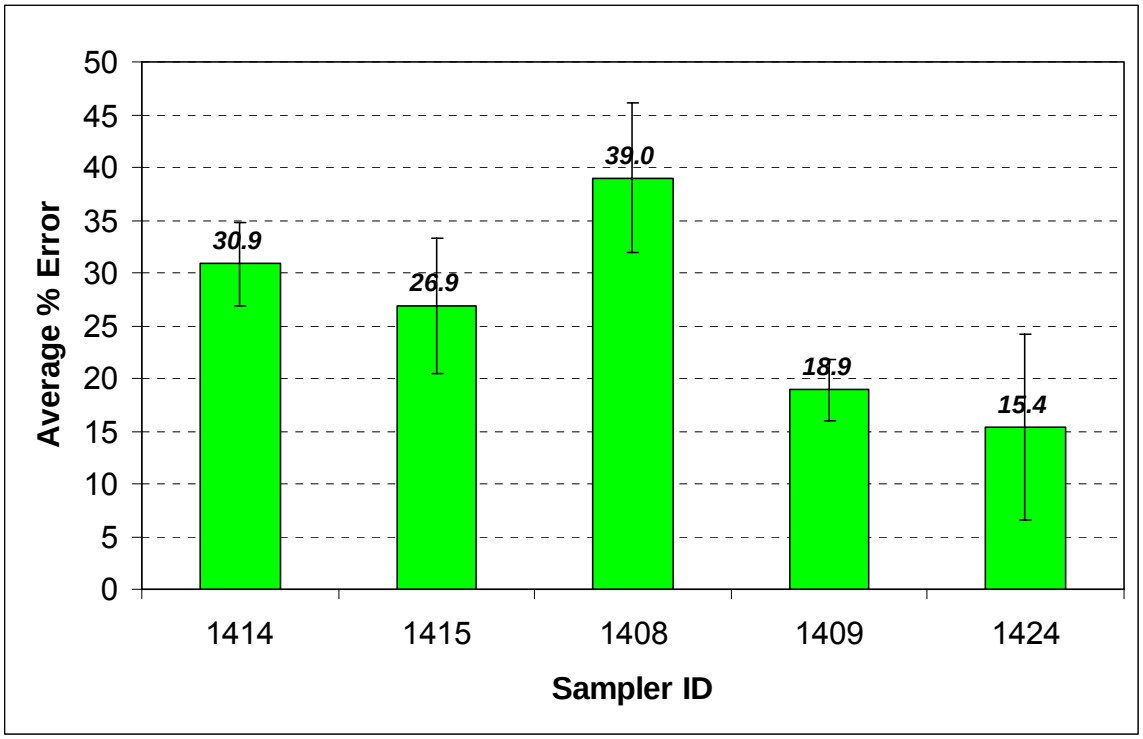

Figure 4. Average percent error for the tested MiniVol samplers when compared to a co-located FRM PM_{10} sampler (error bars represent the 95% confidence interval).

A total of 18 sampling days were observed for the period between October 24, 2002 and February 26, 2003 for the PM_{10} homogeneity study. Out of a potential total sample number of 126 samples (18 sample days x 7 sample sites), 13 (10.3%) individual samples were not obtained due to sampler failure or operator error. Typical explanations included battery failure or errors in setting of the on-board timer/alarm. Typical PM_{10} concentrations observed, as measured at the Logan city site, varied from 4 to 34 $\mu g\ m^{-3}$.

Although some day-to-day variations were observed in the geographical location of PM_{10} maximums, on average, the Cache Valley appeared to be quite homogeneous in terms of relative concentrations. However, at the 95% confidence level, the site located to the north of the Logan city center did show slightly lower PM_{10} concentrations, while the site at the south end of Cache Valley showed slightly higher PM_{10} concentrations. Figure 5 shows the overall average site-to-site PM_{10} concentration variations normalized to the PM_{10} concentrations measured at the Logan (FRM) site. In other words, on any given day, the PM_{10} concentration at any particular site was divided by the PM_{10} concentration measured at the Logan site. This approach was used to minimize potential biases when averaging all of the individual sites' data (e.g. not allowing differences on "low" days to be overshadowed by variations on "high" days). Although distinct trends can be seen in Figure 5, with inclusion of the 95% confidence intervals (error bars), the overall data set shows statistically homogeneous concentrations. For example, error bars

for the Smithfield and American Heritage West (AHW) concentrations overlap the Newton PM_{10} concentration error bars, which, in turn, overlap all of the remaining sites. However, the Smithfield and AHW error bars do not overlap, so their PM_{10} concentrations are statistically different from each other.

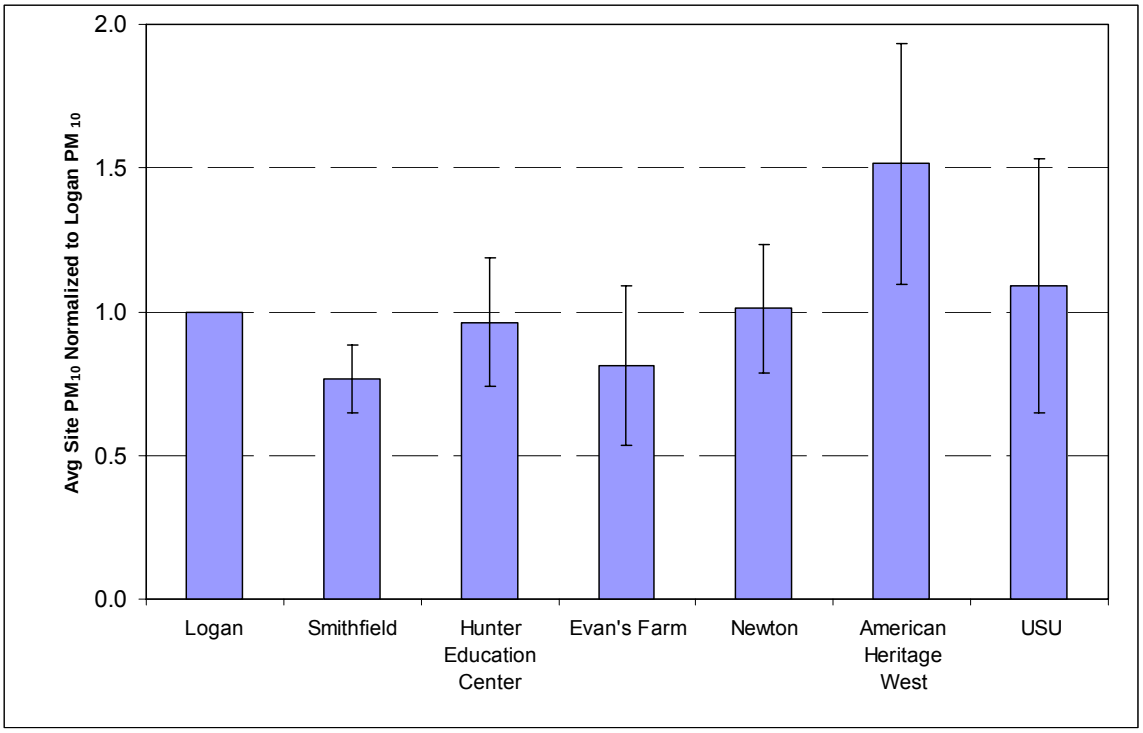

Figure 5. Average PM_{10} concentrations normalized to the observed Logan PM_{10} (error bars represent the 95% confidence interval).

Figure 6 shows the average normalized concentrations in relation to the sampling sites geophysical location. The contours were prepared via Golden Software's Surfer mapping software using a Kriging algorithm. As can be seen, on average there appears to be an identifiable increase in PM_{10} concentrations when moving from the northern end of Cache Valley to the southern end.

Paired PM_{10} and $PM_{2.5}$ samplers were only operated at the Logan and Smithfield locations. From these data, it was found that the $PM_{2.5}$ concentrations were an average of 67.5% ± 6.7 (±95% CI) of the PM_{10} concentrations. More interestingly, the Smithfield $PM_{2.5}$ values averaged 88.4% ± 12.0 (±95% CI) of the Logan $PM_{2.5}$ values, indicating no significant differences between $PM_{2.5}$ as measured at the two sites. This is not unexpected as $PM_{2.5}$ is a subset of the PM_{10} and the smaller $PM_{2.5}$ particles are much more likely to remain suspended in the atmosphere. For example, in still air, the settling velocity of a 2.5 µm diameter particle is sixteen times slower than a 10 µm diameter particle (Cooper and Alley, 2002).

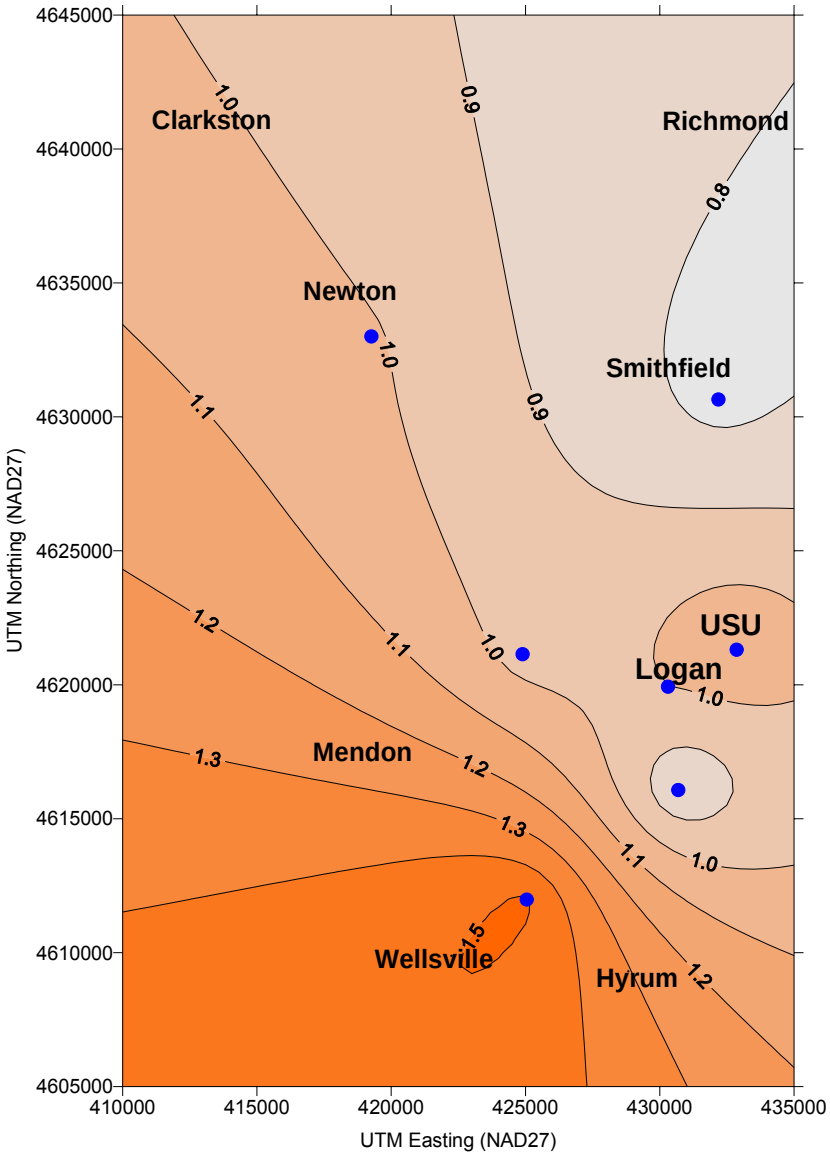

Figure 6. Normalized PM_{10} concentrations measured in northern Utah's Cache Valley, Oct. 2002 – Feb. 2003.

2003/2004 $PM_{2.5}$ Homogeneity (Saturation) Study

Co-location of the MiniVol samplers with the R&P (Logan site) FRM $PM_{2.5}$ sampler showed the portable samplers generally reported similar $PM_{2.5}$ concentrations. As can be seen in Figure 7, the tested MiniVols' measured $PM_{2.5}$ concentrations differed from those reported by the FRM sampler by approximately –21% to +47%. The overall average error was found to be a remarkable –0.9%. Given the magnitude and variability of these percentages and the relative tightness of their individual confidence intervals, the final data analysis calculations for the describe saturation study included the appropriate individual instrumentation correction factors.

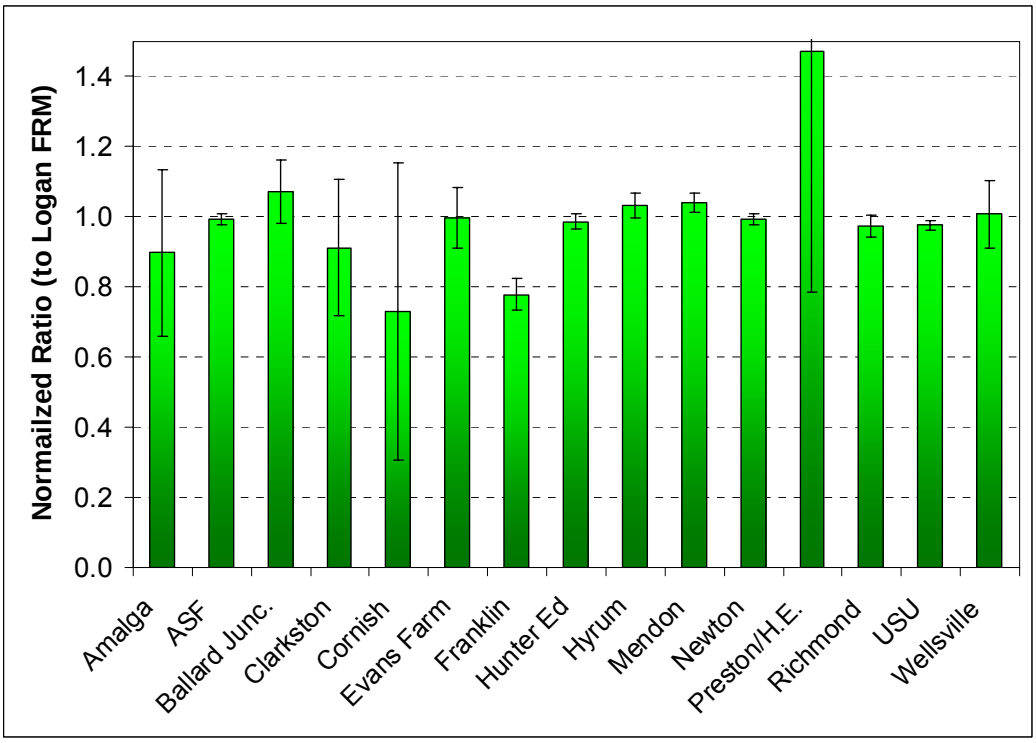

Figure 7. Average percent error for the tested MiniVol samplers when compared to a co-located FRM $PM_{2.5}$ sampler (error bars = 95% confidence interval).

A total of 22 sampling days were observed for the 2003/2004 winter sampling period. Out of a potential total sample number of 374 samples (22 sample days x 17 sample sites), 80 (21.4%) individual samples were not obtained due to sampler failure or operator error. Typical explanations included battery or pump failure, especially during extreme temperature events (< -10ºC), or errors in setting of the on-board timer/alarm. $PM_{2.5}$ concentrations observed during the study, as measured at the Logan city site, varied from 3 to 128 $\mu g\ m^{-3}$.

Similar to the 2002/2003 PM_{10} homogeneity study, the Cache Valley appeared to be relatively homogeneous in terms $PM_{2.5}$ concentrations, although some day-to-day variations were observed in the specific location of $PM_{2.5}$ maximums and minimums. Figure 8 shows the average site-to-site $PM_{2.5}$ concentrations on good-to-moderate days (<65 $\mu g\ m^{-3}$) normalized to the Valley-wide $PM_{2.5}$ concentrations. In other words, on any given day, the $PM_{2.5}$ concentration at any particular site was divided by the overall Valley-wide $PM_{2.5}$ average concentration measured on that day. This approach was used to minimize potential biases when averaging all of the individual sites' data (e.g. not allowing differences on "low" days to be overshadowed by variations on "high" days). This differs from the approach used for the 2002/2003 PM_{10} saturation study, wherein the

concentrations were normalized to the Logan site. The new approach allowed for calculation of confidence intervals about the Logan site as well the other locations.

As can be seen, on the good-to-moderate days, some site-to-site variation did seem to exist; however, with inclusion of the 95% confidence intervals (error bars), the data set shows statistically homogeneous concentrations. For example, confidence intervals for Hyrum and Mendon overlap Evan's Farm and Newton $PM_{2.5}$ confidence intervals, which, in turn, overlap the confidence intervals of the remaining sites. However, the Smithfield and Hyrum error bars do not overlap, so their average $PM_{2.5}$ concentrations on these selected days are statistically different from each other, but not from the data set taken as a whole.

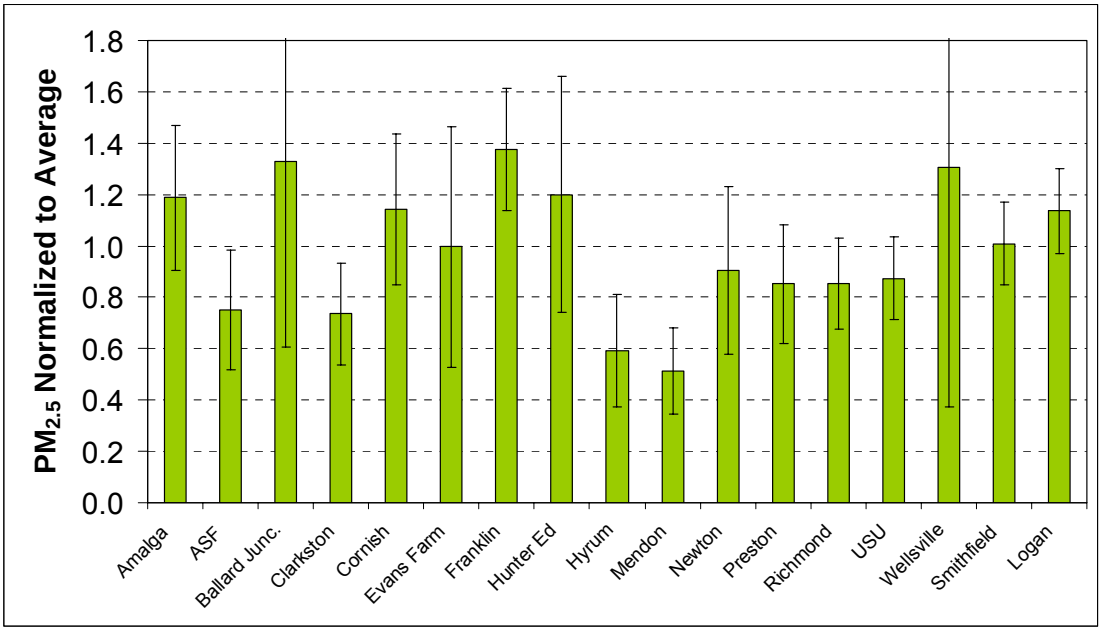

Figure 8. Average $PM_{2.5}$ concentrations normalized to the Valley-wide average $PM_{2.5}$ concentrations on days with $PM_{2.5}$ <65 μg m^{-3} (error bars = 95% confidence interval).

Figure 9 shows the normalized concentrations on days with $PM_{2.5}$ concentrations <65 μg m^{-3} in relation to the sampling sites geophysical location. The contours were prepared via Golden Software's Surfer mapping software using a Kriging curve-fitting algorithm. As can be seen, there appears to be an identifiable trend of increasing in $PM_{2.5}$ concentrations down the center of the Cache Valley, with the highest values recorded in the low population areas of Wellsville, Ballard Junction and Franklin (Idaho), as was also shown in Figure 8.

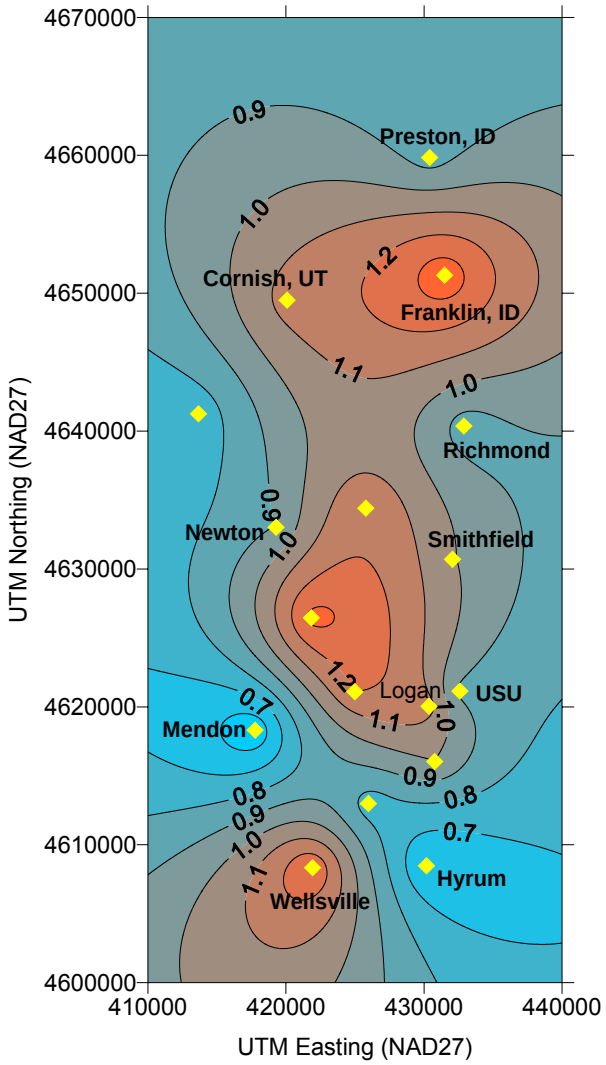

Figure 9. Normalized $PM_{2.5}$ concentrations measured in northern Utah's Cache Valley on good-to-moderate days (<65 µg m^{-3}).

On "unhealthy" $PM_{2.5}$ days (concentrations >65 µg m^{-3}), the data were more varied (larger confidence intervals), but overall more consistent in statistical homogeneity. As can be seen in Figure 10, only the Amalga and ASF sites, located essentially in the middle of the Cache Valley, were statistically different from the average on these high pollution days. Similarly, only the Hyrum and Preston (Idaho) sites, on the far south and north ends of the Valley, were statistically lower than the average. However, once again, taken in its entirety, the data set shows complete statistical overlap or $PM_{2.5}$ homogeneity. It should be noted neither the Ballard Junction or Clarkston samplers successfully operated during any if the high concentration episodes. Also, during these same periods the Newton and Hunter Ed instruments only collected one and two samples, respectively.

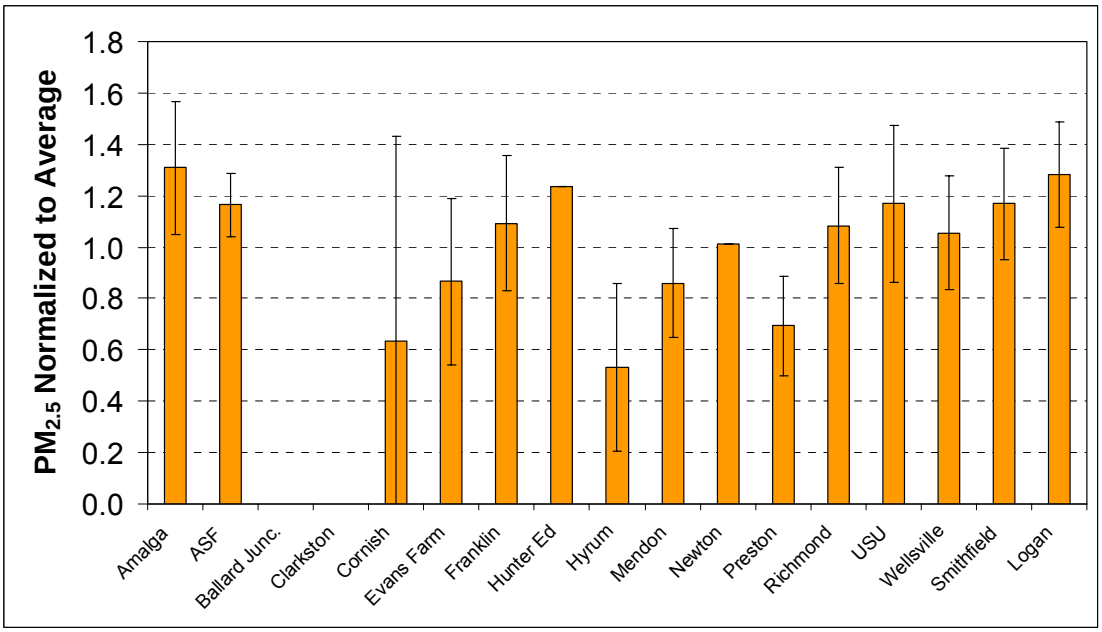

Figure 10. Average $PM_{2.5}$ concentrations normalized to the Valley-wide average $PM_{2.5}$ concentrations on days with $PM_{2.5}$ >65 µg m^{-3} (error bars = 95% confidence interval).

Similar to Figure 9, Figure 11 shows the normalized concentrations on days with $PM_{2.5}$ concentrations >65 µg m^{-3} in relation to the sampling sites geophysical location. As can be seen, there appears to be a more centralized zone of elevated $PM_{2.5}$ concentrations, but that zone encompasses much of the center of the Cache Valley and its main population centers. The lowest average concentrations are found in the southeast (Hyrum) and northwest and north (Cornish, UT and Preston, ID) corners of the Cache Valley.

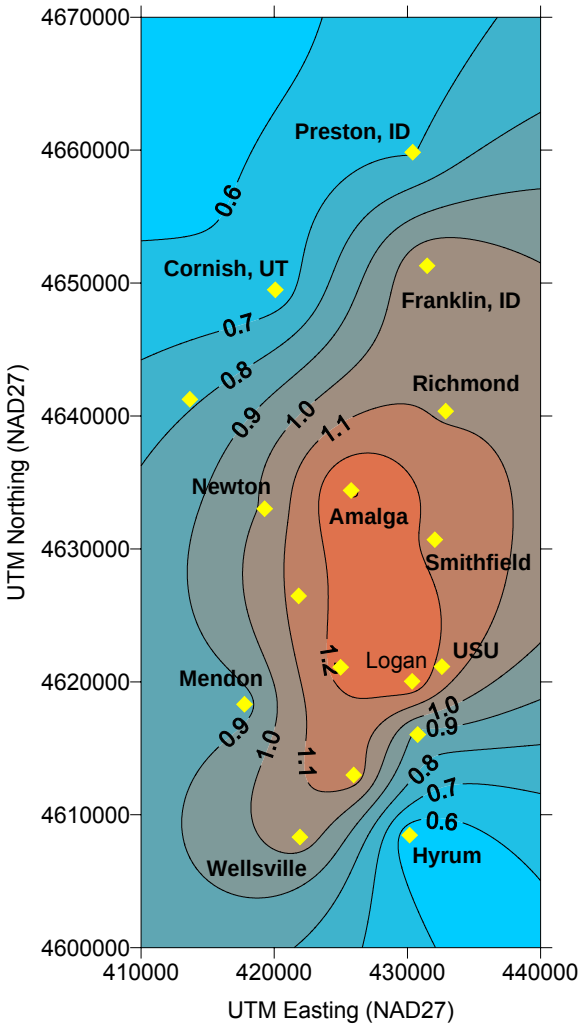

Figure 11. Normalized $PM_{2.5}$ concentrations measured in northern Utah's Cache Valley on "unhealthy" days (>65 µg m^{-3}).

PM_{10} AND $PM_{2.5}$ HOMOGENEITY CONCLUSIONS

From the 2002/2003 PM_{10} saturation study, although some slight areal variations may exist, within in a 95% confidence interval, the wintertime PM_{10} concentrations throughout northern Utah's Cache valley appear to be homogeneous. At the Logan and Smithfield sampling locations, which showed a statistically significant difference in their PM_{10} concentrations, no significant differences were observed in their $PM_{2.5}$ concentrations.

As with the previous winter's PM_{10} study, some site-to-site $PM_{2.5}$ variations were shown to exist; however, within in a 95% confidence interval, the wintertime $PM_{2.5}$ concentrations throughout northern Utah's Cache Valley appear to be homogeneous. On days with 24-hr $PM_{2.5}$ concentrations less then the 24-hr NAAQS (65 µg m^{-3}), the highest concentrations tended towards the center of the Valley, which generally tended to

correspond to the lower elevations of the local topography. On "unhealthy" days or days in which the $PM_{2.5}$ concentrations where greater than the 24-hr NAAQS, the Valley was once again found to be statistically homogeneous. However, during these episodes, the maximum concentration area was much broader and located over most of the population zones on the Utah side of the Cache Valley.

The homogeneity of the PM_{10} and $PM_{2.5}$ concentrations indicates that the particulate issue is not just a problem for the main population center, Logan, but for all of the communities of the Cache Valley. Therefore, the solution to the problem will have to involve all of the surrounding communities

CACHE VALLEY AMBIENT AMMONIA STUDIES

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INTRODUCTION

As was mentioned in the Overall Introduction, the nominal composition of the $PM_{2.5}$ particles in the Cache Valley is dominated by ammonium salts, with ammonium nitrate accounting for 50-95% of the total particulate mass. For comparison, $PM_{2.5}$ in most rural areas in the western United States are typically dominated by total carbonaceous mass and crustal materials (EPA, 2003). Urban areas in the western US, are typically dominated by carbonaceous material; however, nitrate salts appear to be a significant portion of the $PM_{2.5}$ in the southern California area (EPA, 2003). Both rural and urban areas in the eastern US are dominated by the sulfate salts, with a strong contribution from carbonaceous materials (EPA, 2003).

The dominance of secondary, ammonium-based particulate material in the Cache Valley suggested a likely abundance of ambient gas-phased ammonia (NH_3) in the local atmosphere. The strong dependency of the local economy on agriculture, especially livestock production, further supported this supposition. The most current Utah state economic report indicates that Cache Count, UT had total agricultural receipts in 2004 of $121.6 million, with 83.2% of that attributable to livestock production (UGOPB, 2006). The most recent data available for Franklin County, ID (2000) show that agriculture accounted for total cash receipts of $66.0 million, with livestock production accounting for 85.6% of the county's agricultural total (Sonoran Institute, 2006).

In order to investigate levels of ambient, gas-phase NH_3 and whether NH_3 is the limiting factor in NH_4NO_3 formation, an ammonia sampling station was co-located at the Logan city sampling site to establish overall ambient levels of gas-phase and particulate-phase NH_3, as well as the levels of associated anions and cations. Subsequent to this investigation, an additional a program was initiated in the Fall of 2004 to monitor real-time ambient ammonia concentrations at the downtown Logan, UT (urban) location, the site historically used for federal compliance monitoring, and a rural site, located away from significant, typical "city-related" pollutant sources. To be representative of the area, a rural site was sought out, such that it was in the proximity of locally-typical expected rural ammonia sources, such as small cattle operations ("mom and pop" dairies), working agricultural fields, and natural and constructed wetlands. The secondary site chosen was near Amalga, UT. The goal of the second study was to see if the Logan location was representative of valley-wide NH_3 concentrations or if there were significant differences between urban and rural locations.

METHODOLOGY

Ambient Gas- and Particulate-Phase Ammonia and Related Ions

The ambient gas-phase ammonia and acid sampling system was co-located at the Logan city sampling site and sampled on an every sixth day schedule. A URG, Inc. Model 3000C Annular Denuder System (ADS) (URG, 2000) was used for collection of 24-hour averaged gas- and particulate-phase samples. The full system operates at 10 Lpm and consists of a sharp-cut $PM_{2.5}$ cyclone, followed one or two acid gas (Na_2CO_3-

coated) denuders, followed by the NH_3 gas (citric acid-coated) denuder, followed by a 2-stage filter pack assembly. For the purpose of this study, the sampling was initiated in October of 2002 and continued through the end of 2003.

The NH_3 collection denuders were prepared prior to exposure by coating the inner surfaces with a 1% citric acid solution (1.0 g citric acid, 99 ml of methanol, 1 ml glycerol). For acid gas collection, 1% Na_2CO_3 solutions were prepared from 1.0 g Na_2CO_3, 1.0 g glycerol, 50 ml double-distilled, deionized water (DDW) and 50 ml methanol. Glycerol was used to make the denuder surface more adhesive and prevent oxidation of nitrite to nitrate by ozone. Within the ADS, air was drawn through the cyclone for large particle removal, then through the Na_2CO_3-coated denuder where acid gases were collected, and then through the citric acid-coated denuder where NH_3 (g) was absorbed to the walls. The air stream was then drawn through a filter pack to collect the particulate matter for mass and compositional determination, followed by the nylon backup filter. The system was enclosed in a weatherproof box, which was kept at a lower limit of 7 ^{0}C if the ambient temperature was less than 7^{0}C, or 2^{0}C above ambient temperature if the ambient temperature was greater than 7^{0}C. The system was connected to a pump with an accompanying mass flow controller and a dry gas meter. The mass flow controller allowed precise control of airflow through the annular denuder/cyclone assembly. The Gallus 2000 dry gas meter (Schlumberger, Reims Cedex, France) was also plumbed to the system and was calibrated before use to insure precise sample volumetric reading.

After exposure, the denuder tubes were separately eluted with 10 ml (NH_3) and 30 ml (acid gases) of double-distilled, deionized water. Additionally, 10 µL of concentrated H_2SO_4 was added to the NH_3 extract to acidify the sample, ensuring the collected gas-phase ammonia (NH_3) would remain in solution as the more soluble ionic species, ammonium (NH_4^+). The samples were stored in the dark at 4ºC until the extract concentrations were quantified via ion chromatography. The Dionex IC system consisted of the following equipment: AS 40 Automated Sampler, CD 20 Conductivity Detector, GP 40 Gradient Pump, Membrane Suppressor, LC 25 Chromatography Oven, and an IonPac® AS4A-SC (4 mm) anion column or an IonPac® CS12A cation column, AG-4ASC anion guard column or CG12A cation guard column, depending on the ionic species of interest.

For anion analysis from the denuder washes, a 25-µL injection loop was used in the IC, while for cations analysis from the denuder washes, an 80-µL injection loop was used; and for filter extraction cations, a 195-µL loop was used. This was because the concentration of filtered extraction cations was much lower than that from denuder washes, and a larger loop allowed injection of more sample onto IC which allowed more consistent peak detection. For anions analysis, DDW filtered through a 0.2 µm filter was used as reagent water and 1.7 nM sodium bicarbonate and 1.8 nM sodium carbonate solution as the eluant. Stock standard solutions of 1000 mg/L of $C1^-$, NO_3^-, NO_2^-, SO_4^{2-} were prepared from ACS reagent grade salts (Fisher, Fair Lawn, NJ). For cations analysis, 0.15 M H_2SO_4 was used as the eluant. Stock standard solutions of 1000 mg/L of Na^+, K^+, Mg^{+2}, Ca^{+2}, NH_4^+ were prepared from ACS regent grade materials.

Calibration curves were prepared using 1, 5, 10 mg/L (ppm) stock standard solutions and were verified on each working day and after approximately 20 samples. Blank and continuing calibration verification standards (CCV), such as 5 ppm standard anions or cations solutions, were tested approximately every 10 samples. Peak identification and data processing were performed using Dionex PeakNet Data Chromatography software (Version 2.0). Ambient air concentrations were calculated from the IC analytic results and sampled air volume.

Urban vs. Rural Ambient Gas-Phase Ammonia Study

This study began in November 2004 and went through April 2005, gapping the typical Cache Valley $PM_{2.5}$ "season". It should be mentioned that due to equipment problems the Logan city NH_3 system, sampling did not actually begin until Dec. 7, 2004. ThermoEnvironmental Instruments Model 17C Chemiluminescent Ammonia Analyzers were installed in climate controlled sampling trailers at the Logan site (41.7309°N, 111.8376°W, ele. 1380 m asl) and at a newly established site near Amalga, UT, approximately 15.1 km northwest of the Logan site, roughly near the center of the Utah portion of the Cache Valley. Within 3 km of the rural site are a number of agricultural fields, two small dairy operations (50-100 cows each), natural wetlands and an associated stream system, a waste lagoon, and a small cheese factory. The rural site specific coordinates are as follows: 41.8584°N, 111.8943°W, ele. 1355 m asl. All UTMs given are in NAD27 coordinates.

At both locations, sample air was transferred into the analyzers through glass sampling manifolds and Teflon® tubing. The Model 17C Analyzers operate through the sequential measurement of NO, NO_2, and NH_3 via ozone initiated chemiluminescence and surfaced catalyzed oxidation of the ammonia. The system first measures ambient NO and NO_2 as describe by typical federal reference method gas-phase chemiluminescence (40CFR50, App. F, 2006), as such the NO_x data are archived and available as well as the ammonia. The NH_3 analyzer adds an additional 775°C stainless steel converter to oxidize the NH_3 to NO. The 17C then measures the additional system response due to the newly created NO, which is then reported as ambient ammonia (TECO, 2004).

The instruments were calibrated or zero/span checked on an at least semi-weekly basis using commercially-purchased ammonia and zero gas standards. The instrument has a reported lower detectable limit of 1 ppb, a response time of 120 seconds, and a linearity of ±1% at ranges up to 20,000 ppb (TECO, 2004). Similar instrument characteristics were also reported via a separate independent study (Cowen et al., 2004). Additional operational details can be found at the manufacture's website (TECO, 2006).

RESULTS AND DISCUSSION

Ambient Gas- and Particulate-Phase Ammonia and Related Ions

Figure 12 shows the ambient, gas-phase ammonia concentrations measured at the Logan site from October 2002 through December 2003. The average overall concentration is 9.3 ppb ± 1.2 (95% CI). The minimum NH_3 concentrations were around 2.5 ppb, which were observed in the summertime, and the maximum concentrations approached 25 ppb, which were observed in the wintertime. This is well above what is typically considered tropospheric background levels (0.05 – 0.2 ppb) and compares to other areas of high agricultural activity (Robarge et al., 2000; Finlayson-Pitts and Pitts, 2000). The elevated ammonia levels are not unexpected due to the enclosed nature of the Valley's airshed, especially during wintertime inversion episodes, and the common nature of livestock production in the local region.

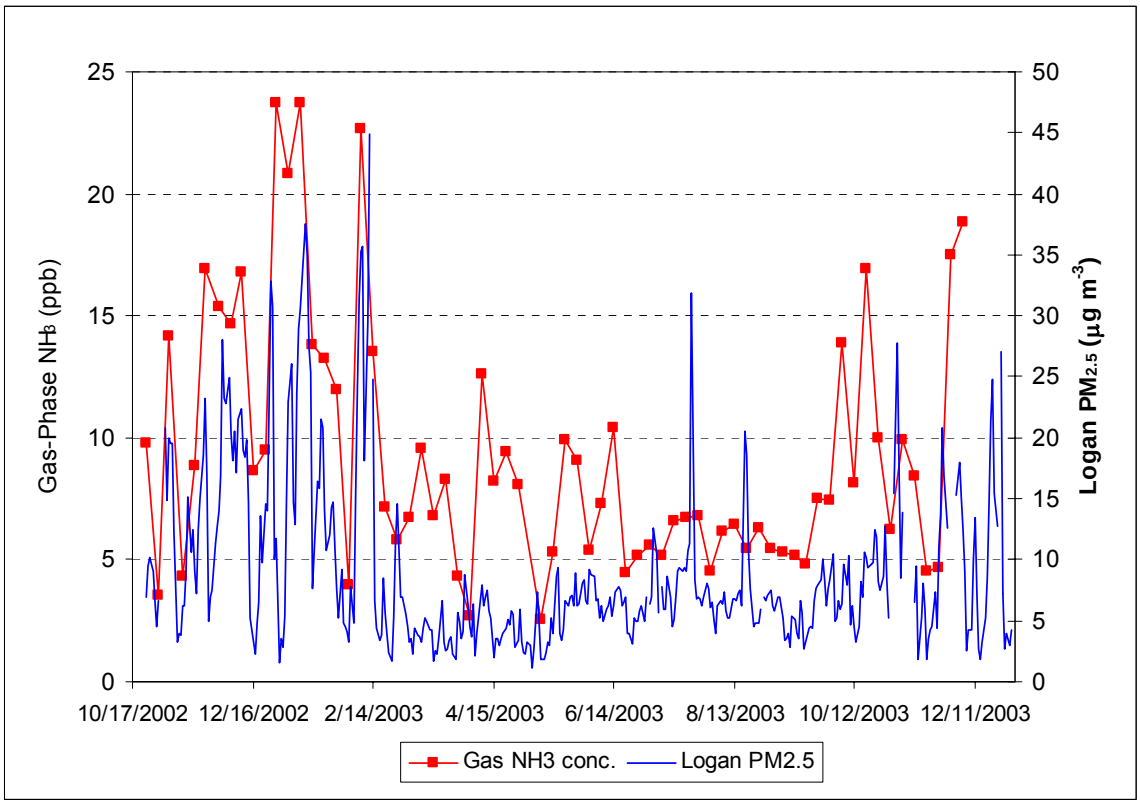

Figure 12. Ambient NH_3 and $PM_{2.5}$ measured in Logan, Utah.

Based primarily on the number of livestock in the Cache Valley, the Utah DAQ estimates daily (wintertime) emissions on the order of 4.8 metric tons (UDAQ, 2006). It is well recognized that current NH_3 emissions algorithms are considered highly uncertain (CAEAAFO, 2002; CENR, 2001; FAO, 2001); however, examination of these first order emissions estimates can give some insight into local atmospheric photochemical particle formation. The Utah DAQ has also estimated daily NO_x and SO_x emissions at 8.3 and 8.5 metric tons. Based on these numbers, there is easily enough available gas-phase NH_3 to neutralize the emitted SO_x. However, the NO_x-NH_3 particle conversion is more accurately represented as an equilibrium reaction, and as such, complete conversion would not be expected. Furthermore, the resultant ammonium nitrate particle formation

is favored during cold and humid (i.e. foggy) conditions as experienced during the Cache Valley's winter months. The high ambient NH_3 concentrations suggest the NH_3 is in excess and the emission estimates of all of the noted species may need to be revised.

The concurrent $PM_{2.5}$ concentrations from the Logan site are also shown in Figure 7 and it appears that the two parameters may be correlated. Linear regression analysis shows only a moderate correlation ($r^2 = 0.537$); however, it can be said that the higher $PM_{2.5}$ concentrations typically occurred during periods of elevated ambient ammonia. Further, the regression analysis proportionality constant, the "slope" term, is very nearly equal to unity (1.006), suggesting that in the local area, a 1 ppb increase or decrease in ambient NH_3 would be paralleled by a similar change in the $PM_{2.5}$ concentration. This is not to suggest that NH_3 emissions, and thereby particulate ammonium nitrate, increase in the winter months. More likely these increases are related to seasonal decreases in the atmospheric mixing volume and dilution rates.

On a seasonal basis, the winter months (Dec., Jan., Feb.) showed the highest NH_3 concentrations, averaging 13.9 ppb ± 2.99 (95% CI), which was statistically different from the remaining three seasons (see Figure 13). The spring (Mar., Apr, May), summer (Jun., Jul., Aug.) and fall (Sept., Oct., Nov.) NH_3 concentrations were not significantly different from each other. The overall average ambient NH_3 concentration for these three seasons was 7.7 ppb ± 0.94.

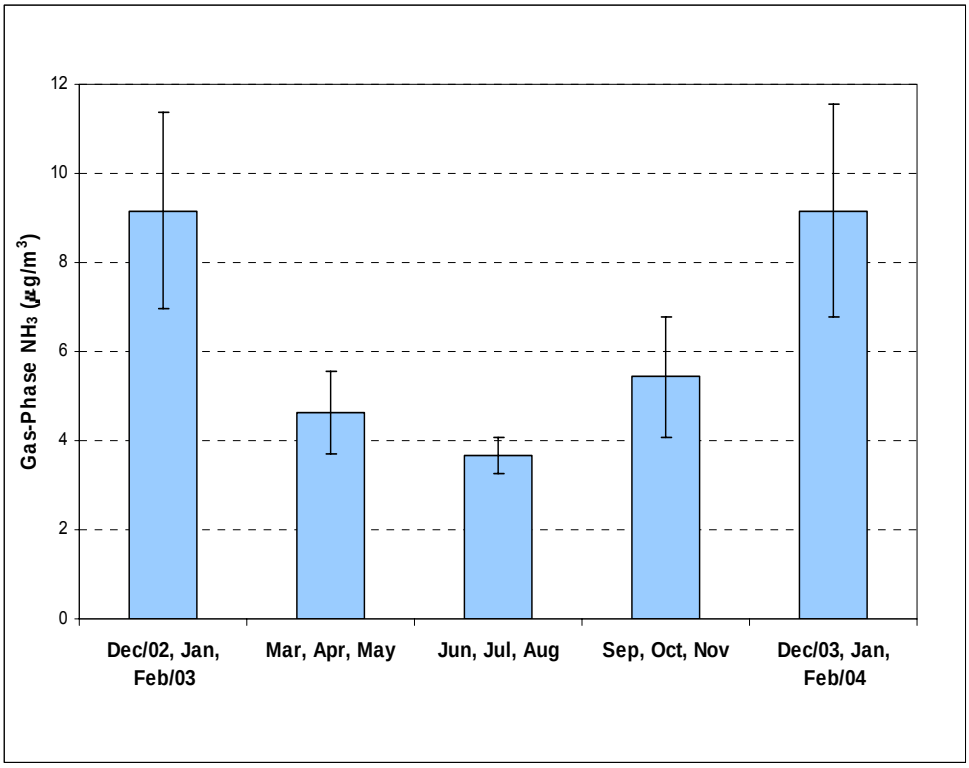

Figure 13. Seasonal variations of Cache Valley gas-phase ammonia (error bars represent 95% confidence intervals).

In order to more fully examine whether the gas-phase NH_3 is in abundance or deficit in relation to potential formation of particulate ammonium nitrate, three separate algorithms were applied to the collected ionic concentration data. The models used were the excess NH3 model of Blanchard et al. (2000), the particulate-to-total NO_3^- ratio model also by Blanchard et al. (2000), and Gas Ratio Analysis (free NH_3 to total HNO_3) model of Ansari and Pandis (1999). The details of these models, and their accuracy compared to more detailed atmospheric photochemical models, are given in the associated references, but in brief they all attempt to model the gas- and particulate phase ion balance. The average results of these three individual calculations can be seen in Figure 14.

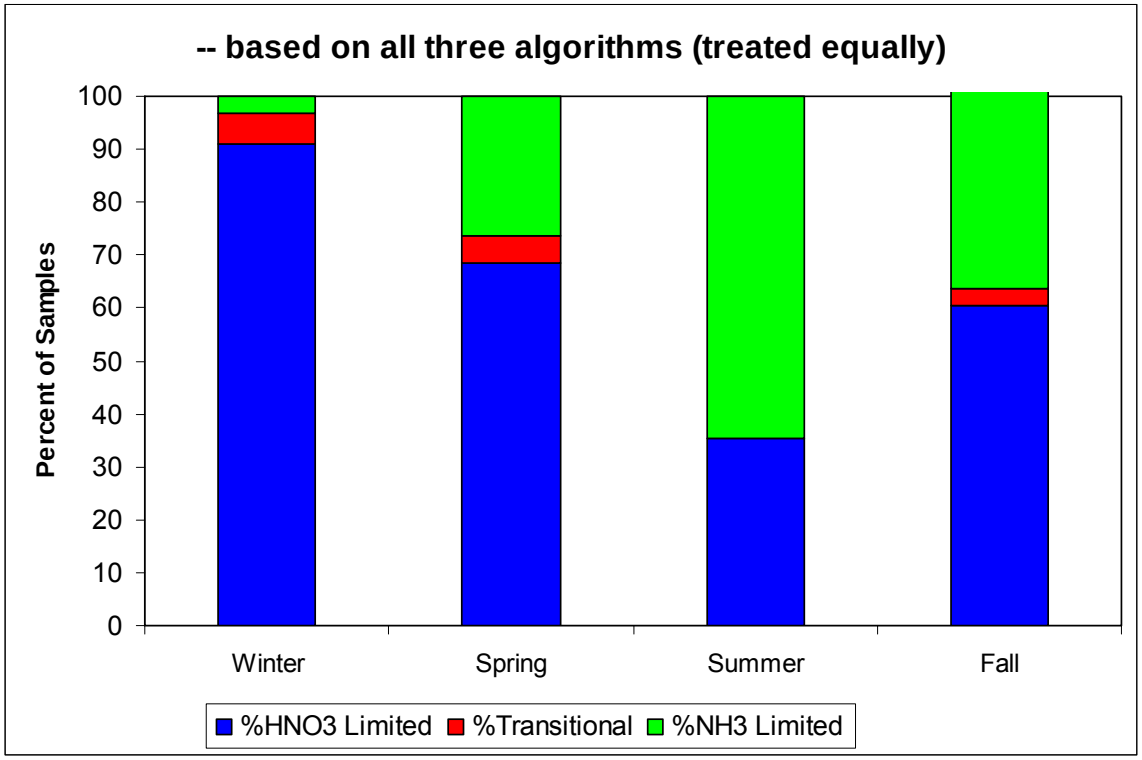

Figure 14. Seasonal determination of HNO3- or NH3-limited particulate ammonium nitrate formation.

As can be seen, during the critical wintertime periods, the NH_4NO_3 formation was limited by the availability of ambient nitric acid (HNO_3) for approximately 90% of the observed samples. Although not relevant to the Cache Valley's elevated wintertime $PM_{2.5}$ concentrations, the two of the three remaining seasons also should NH_3-rich (HNO_3-limited) atmospheres. Examination of the specific ionic concentrations and the particulate ammonium salts further suggest that the wintertime gas-phase NH_3 is in excess by as much as a factor of two (2x). More complete discussion of the above analysis can be found in Zhu (2005), and is presently in preparation for publication in a peer-reviewed journal.

Urban vs. Rural Ambient Gas-Phase Ammonia Study

As shown in Figure 15, the ambient NH_3, as measured at both the Logan (urban) and Amalga (rural) sites followed similar trends and paralleled elevated and depressed periods with the measured $PM_{2.5}$ concentrations. The Logan ammonia concentrations showed a moderate linear regression correlation with the collocated $PM_{2.5}$ concentrations with an R^2 value of 0.6543. The rural (Amalga) was statistically less well correlated showing an R^2 value of 0.4895. However, directly comparing the ambient ammonia concentrations between the two sites showed a correlation coefficient of 0.8255, with a proportionality constant of 2.5 and an intercept of 7.6 ppb (using the Logan concentration as the independent variable), indicating the rural ammonia concentrations were approximately 2½ times the average urban values.

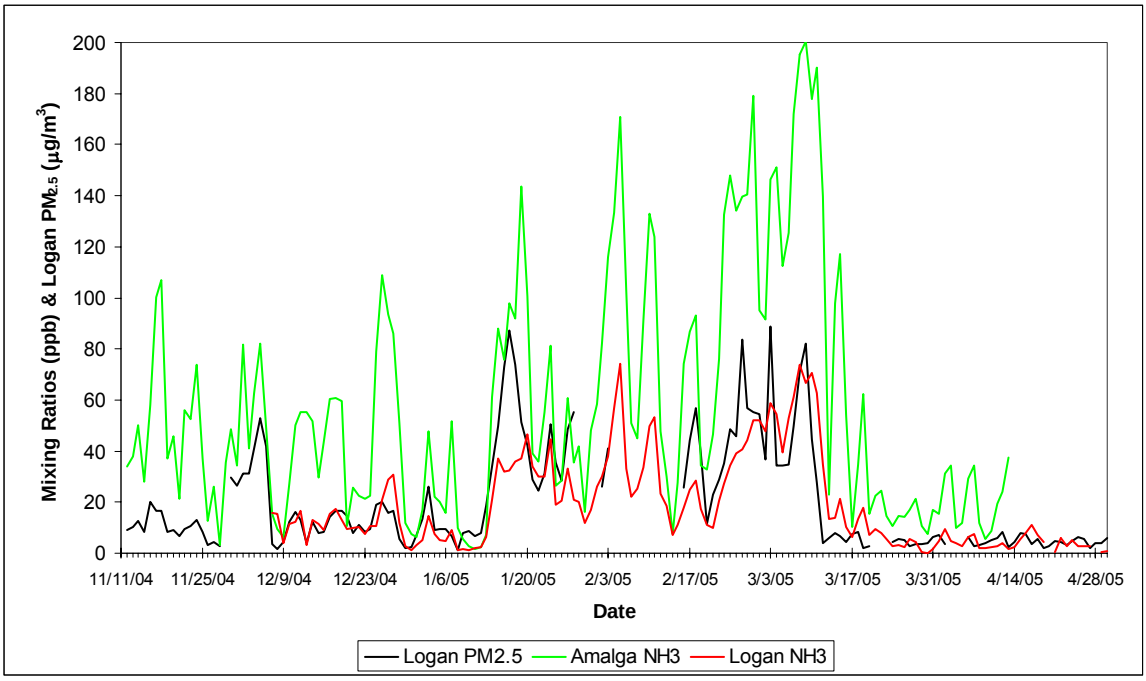

Figure 15. Logan and Amalga ambient NH_3 (24-hr avg) compared to Logan $PM_{2.5}$ (24-hr avg).

As can also be derived from Figure 15, the Logan site recorded a maximum 24-hr average value 74 ppb and a minimum value of <1 ppb, with a period daily average value of 19 ppb. This average value is remarkably consistent with that reported by Martin and Zhu (2004), 14 ppb, for the Logan location over the previous two winters using the previously described separate, denuder tube technique. The Amalga location showed much higher concentrations, with maximum, minimum, and average values of 200 ppb, 1 ppb, and 58 ppb, respectively. It is of interest to note that at the Amalga location, 1-hr average values >200 ppb were not unusual, particularly during strong inversion events and the maximum 1-hr NH_3 concentration observed was 373 ppb.

At the 95% confidence interval, the monthly ambient ammonia averages at the rural (Amalga) site were statistically higher than the concentrations observed at the urban (Logan) location (see Figure 16). This difference is believed to be due to the relative abundance of NH_3 sources near the rural location, and the increased likelihood of local photochemistry due to the increased presence of possible reactants at the urban site (NOx, VOC, etc.) due to increased nearby pollutant sources (especially automobile traffic). As with Figure 15, Figure 16 also shows the highest NH_3 concentrations occurred in January and February, when persistent inversions where present and high $PM_{2.5}$ concentrations were observed.

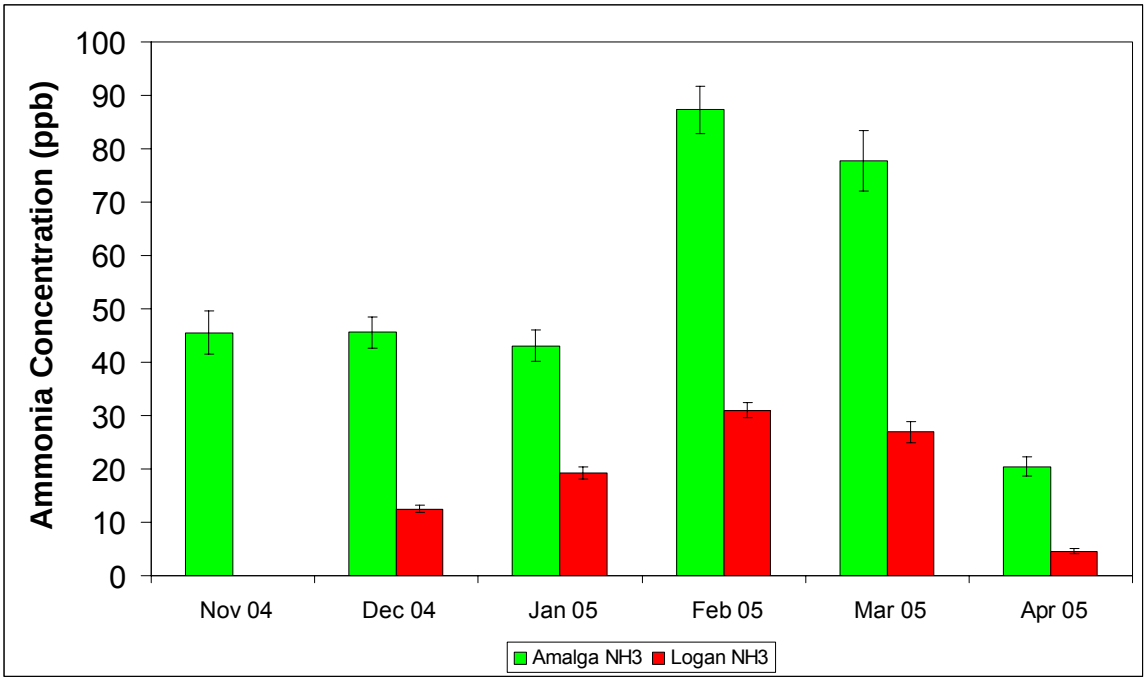

Figure 16. Monthly ambient ammonia averages for Logan (urban) and Amalga (rural), UT.

As can be seen in Figures 17 and 18, both the Logan and Amlaga NH_3 displayed noticeable diurnal patterns, with maximums typically occurring the morning hours (6 am to 10 am MST) and the minimum usually in the mid-afternoon to early evening (2 pm to 6 pm MST). The hour-to-hour diurnal difference appeared stronger, particularly at the rural location, when the ambient concentrations were at their highest in February and March.

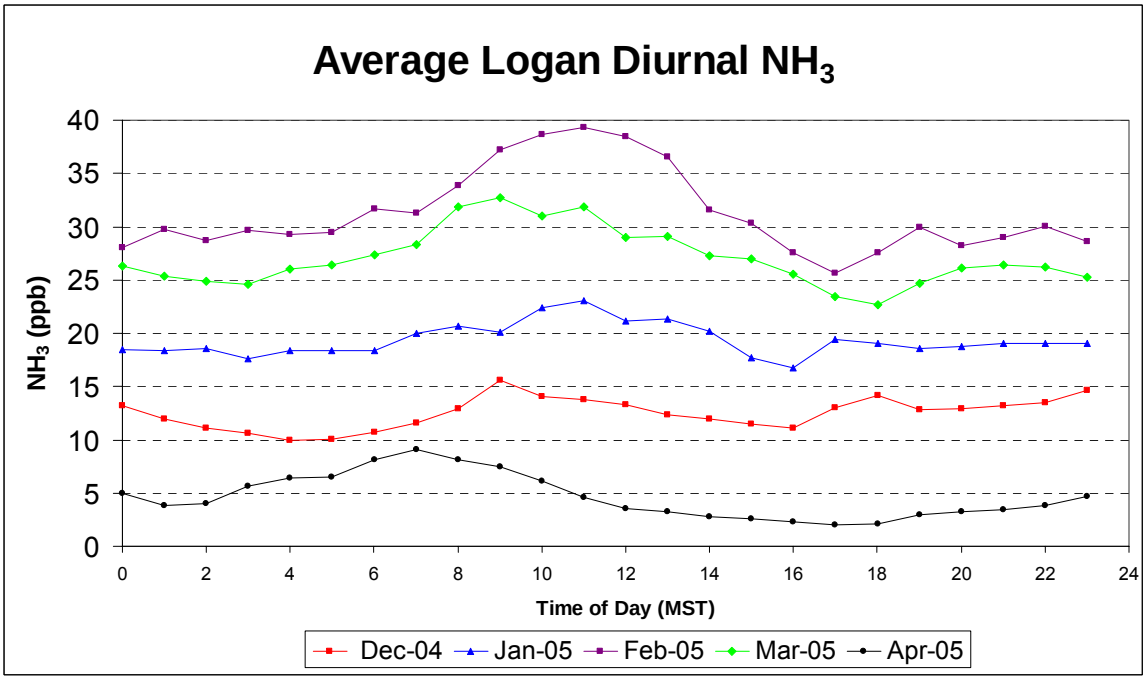

Figure 17. Logan (urban) diurnal ambient ammonia behavior.

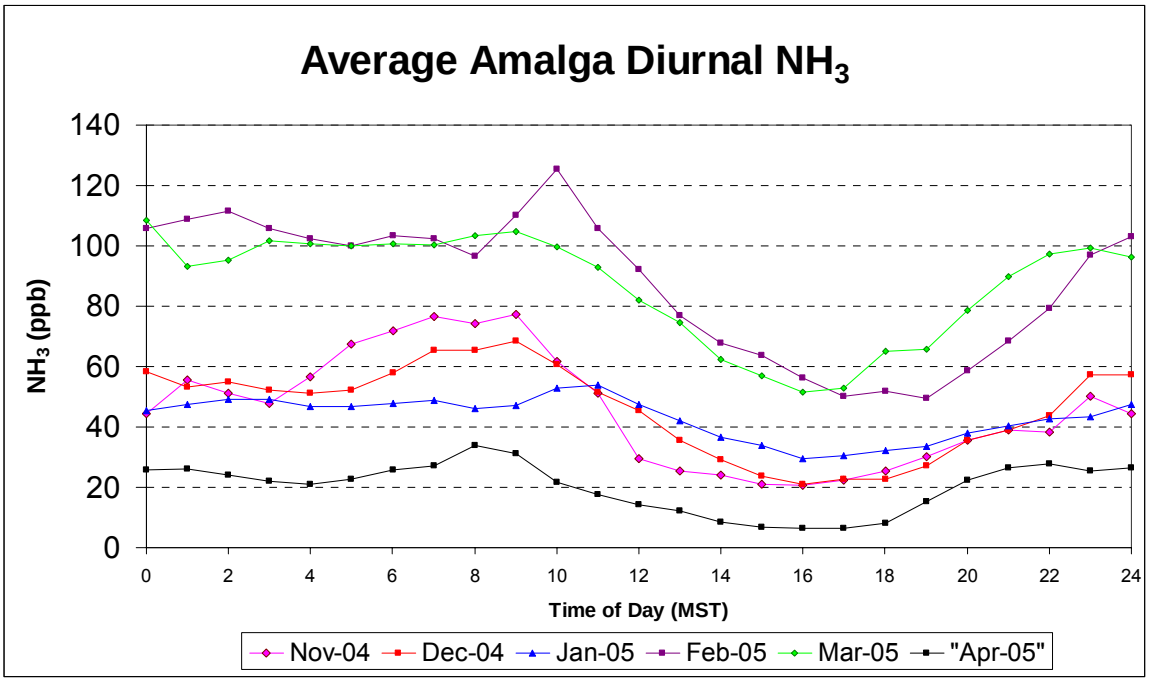

Figure 18. Amalga (rural) diurnal ambient ammonia behavior.

The abundance of ambient NH_3 at the rural location suggested that the site may be significantly impacted by an adjacent ammonia source. However, examination of observed NH_3 concentrations as a function of wind direction showed that the ammonia sources in the rural location seemed ubiquitous and the concentrations were consistent from most wind directions (see Figure 19). Furthermore, the data, averaged for wind direction, show complete statistical overlap (at the 95% confidence interval) within any given month. It should be mentioned; however, that during February and March, the average observed concentrations from the east and southeast, respectively, were statistically higher than some, but not all, of the other wind directions. While the previously mentioned cheese factory is approximately 1.4 km to the south-southeast, the land to east is mostly pasture land, agricultural fields, and natural wetlands/river areas. The dominant wind directions during the study period were north or northeast and south, southwest, or west, roughly following the topographical confines of the valley.

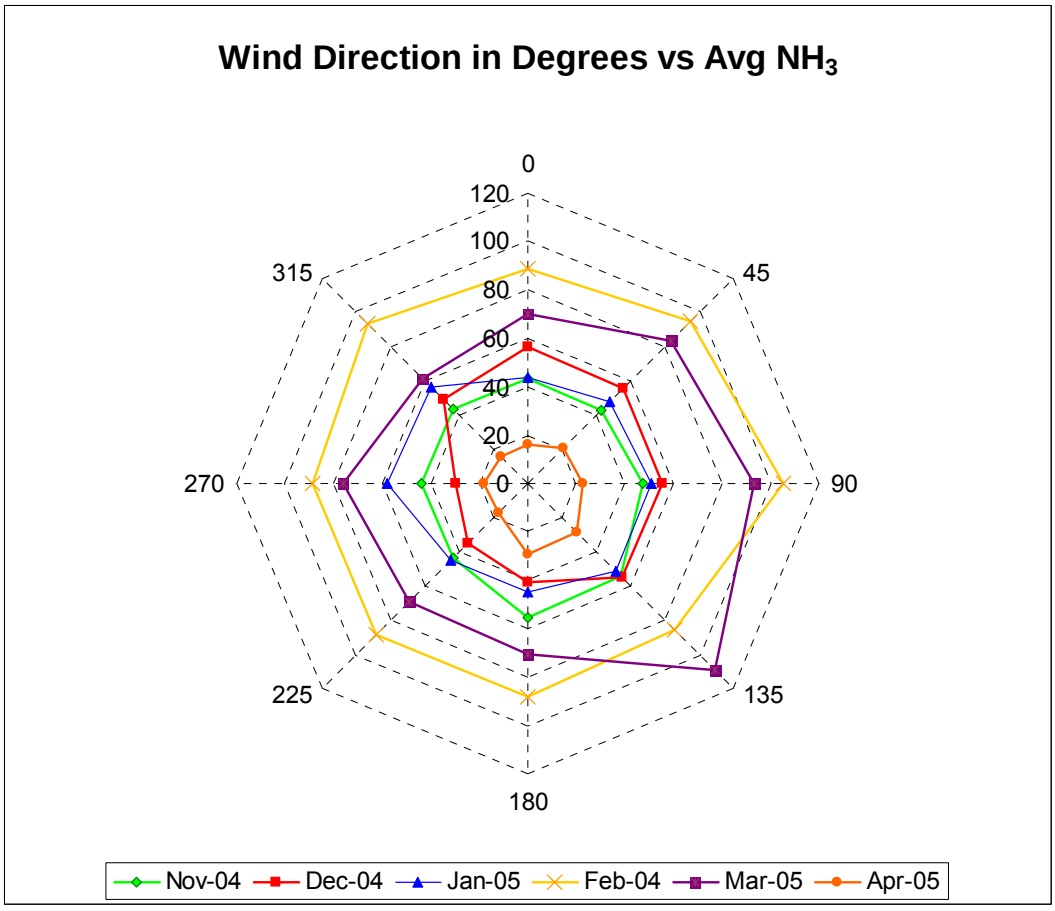

Figure 19. Amalga (rural) NH_3 concentrations as a function of wind direction.

AMBIENT AMMONIA CONCLUSIONS

Concentrations of ambient gas-phase ammonia reached values as high as 25 ppb during winter inversions, but averaged closer to 14 ppb. The gas-phase NH_3 concentrations in the two observed winter periods (2002/2003 and 2003/2004) were almost same, suggesting consistent pollutant wintertime emission rates and similar inversion-dominated pollutant trapping. Spring, summer, and fall NH_3 concentrations were significantly lower, averaging just over one half of the wintertime levels. The data showed only a moderate relationship between ambient NH_3 and $PM_{2.5}$ ($R^2 = 0.537$), but the overall trend suggested a one-to-one rate of change between the two parameters.

Applying an excess ammonia model, a particulate-to total-NO_3^- model and gas-ratio model, showed that all the of results indicated the Cache Valley's wintertime atmosphere was ammonia-rich or HNO_3-limited in reference of secondary NH_4NO_3 aerosol formation (using the Logan site as the refence location). Since Cache Valley's atmosphere has been proved to be ammonia rich, or HNO_3-limited through the herein described study, reduction on HNO_3 will produces a greater, more immediate, reduction of aerosol NH_4NO_3 than will an equivalent reduction of NH_3. Programs to be implemented could include vehicle inspection and maintenance (I&M) programs, increased public transit programs, car pooling, and other programs to reduce vehicle miles traveled.

The monthly average ambient ammonia concentrations at the urban varied from 5-31 ppb, with the highest values occurring in February and March, the same time periods when maximum $PM_{2.5}$ concentrations were observed. The highest daily average observed was 74 ppb and the test period (five month) average was 19 ppb. These values compare well to previous investigators reported values for the Logan area (Martin and Zhu, 2004; Mangelson et al., 1997) and are generally much higher than those reported for other urban areas, with the exception on Phoenix, AZ (Watson et al., 1994) and Riverside, CA (Yoong, 1981). The listed two urban areas reported ambient NH_3 concentrations on the same order as the Logan site.

The nearby rural (Amalga) site showed monthly average ammonia concentrations of 20 to 87 ppb, with the highest values occurring during the same months as those at the urban site. The overall correlation (R^2) between the two sites was 0.8255, with a derived relationship between locations as shown in Equation 1:

$$[NH_3]_{Rural} = 2.51 * [NH_3]_{Urban} + 7.58 \qquad \text{(Equation 1)}$$

where all concentrations are in parts per billion (ppb).

The highest daily average observed at the rural was 200 ppb and the test period (six month) average was 58 ppb. The maximum 1-hr NH_3 concentration observed for the rural location was 373 ppb. These values are well above those reported for non-agricultural, rural areas (Watson et al. 1994; Pryor et al. 2001; Thoni et al. 2003), but are

in line with rural sites collocated around strong agricultural production facilities (Mopunt et al., 2002; McCulloch et al., 1998).

Comparison of hourly ambient NH_3 concentrations with hourly averaged wind directions showed near complete statistical homogeneity, although there were a few direction-to-direction differences during the months of February and March. The independent nature of the ammonia concentrations in relation to the wind vectors suggests that the rural NH_3 sources are well-dispersed throughout the Cache Valley and it is likely the no single source (no one point, area, etc. source) dominates the local NH_3 emissions budget. It would seem more likely the high rural ammonia concentrations are due to a multitude of valley-wide sources.

Additionally, as shown in Equation 1, the rural ammonia levels are on the average 2.5x greater than the urban levels. As also mentioned above, as measured at the Logan site alone, was in ammonia excess by a factor of approximately two in regard to the photochemical formation of particulate ammonium nitrate. If indeed the Amalga location is representative of the other rural areas of the Cache Valley, the local atmosphere may be more ammonia-rich than previously assumed. This would, in turn, mean that the worth of potential NH_3 reduction scenarios would have to be very carefully examined.

ON-ROAD VEHICLE EMISSIONS IN CACHE VALLEY (2004)

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INTRODUCTION

Research described within the ammonia section of this document showed that the local Cache Valley ambient air is ammonia-rich during the winter months, meaning that the limiting compound is the nitric acid (HNO_3) that combines with the gaseous ammonia (NH_3) to form NH_4NO_3. Nitric acid is photchemically formed in the atmosphere from precursor oxides of nitrogen (NO_x) compounds through a series of photochemical reactions involving other reactants such as ozone (O_3), hydroxyl radicals (OH), reactive volatile organic compounds (VOCs), and available solar radiation (insolation). The main source of NO_x and VOCs in Cache Valley is the transportation sector with over 80,000 vehicles registered in Cache County, UT and Franklin County, ID. The Cache County Assessor lists approximately 67,000 motor vehicles, half of which are 1995 or older, as being registered within the county (Cache County, 2004). Franklin County, ID, as of 2004, had 12,900 total registered motor vehicles of similar age structure (IDT, 2006).

A potentially effective way to control NO_x and VOC emissions is to control the emissions from automobiles, and this is typically accomplished through the implementation of an Inspection and Maintenance (I & M) Program that tests emissions on an annual or bi-annual basis. Vehicles that do not pass the test must be fixed before being allowed to register. This option for controlling pollutant emissions is currently being considered by Cache County, but information was lacking on what expected emissions of the current vehicle fleet and what fraction of the fleet may be expected to fail or pass an I & M Program. As such, a series of on-road emission tests were performed in May 2004 in and around Logan, UT.

METHODOLOGY

The vehicle emission testing was done using an MD-LaserTech RSD (remote sensing device) borrowed from Utah County. Additionally, a trained operator, Todd Rittle, from the Utah County Department of Health was on hand to operate and calibrate all of the test equipment. In brief, the system shot infrared and ultraviolet laser beams across a roadway, reflected of a polished mirror and returned to the transceiver, where wavelength-specific energy absorption was recorded. The concentrations of NOx, VOCs, CO, and CO_2 within the vehicle plume were the instrumental correlated with the laser attenuation. Additional information recorded included vehicle speed, acceleration, and license plate data (the latter recorded via a time-marked photograph. It should also be noted that a beam height of approximately 14" was selected, knowing this be height was a choice between measurement of typical car or typical pickup exhaust heights. The 14" was more typical of the passenger automobile.

The testing occurred at various roadside sites along high traffic areas throughout Cache Valley during the period of May 13-20, 2004. A relative map of the tested locations can be seen in Figure 20. Finally, the slope of the road at each site was subsequently measured by USU undergraduate Environmental Engineering students using standard surveying techniques and used to calculate a comparison parameter known as vehicle specific power (VSP).

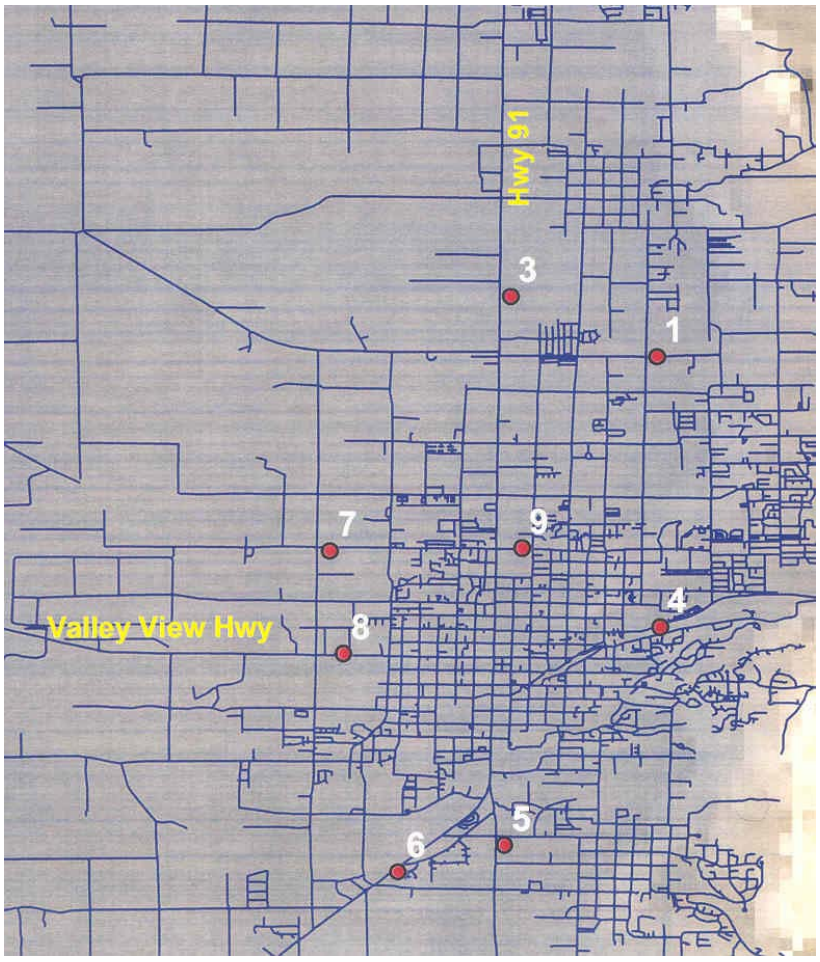

Figure 20. Locations of May 2004 Cache Valley on-road vehicle emissions study.

RESULTS AND DISCUSSION

The number of (valid) vehicles surveyed for exhaust emissions at all sites within Cache Valley was 12,464 at an average speed of 34.4 mph. The vehicles were separated into bins by vehicle year beginning with the year 1980 and continuing at five year increments until the last bin of 1996 and older. Figure 21 displays how the sample set of surveyed vehicles sorted by vehicle year compares with the total number of registered vehicles in the county also sorted by vehicle year. The two curves in this figure are very similar suggesting that the sampled data is a good descriptor of the general vehicle population.

Figure 22 shows the percentage of the total bin population represented in the sampling set. The majority of registered cars in Cache County have a vehicle year of 1990 or greater, and this division can be seen in Figure 22 as the 1990-95 and older than 1996 bins had the greatest percentage of total cars sampled.

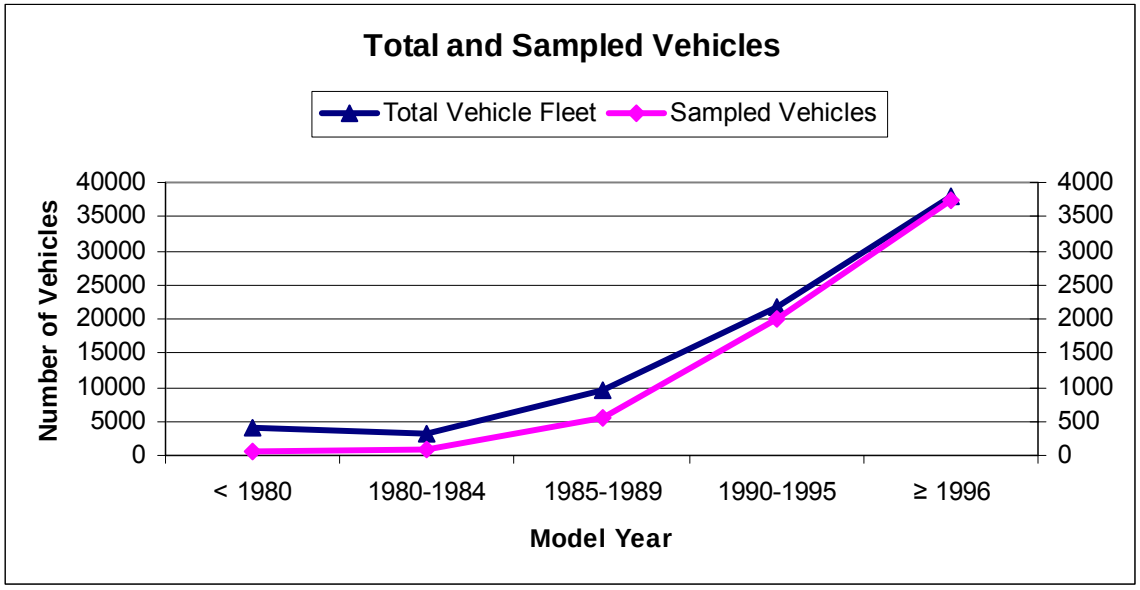

Figure 21. Vehicles surveyed with compared to total Cache County registered vehicles.

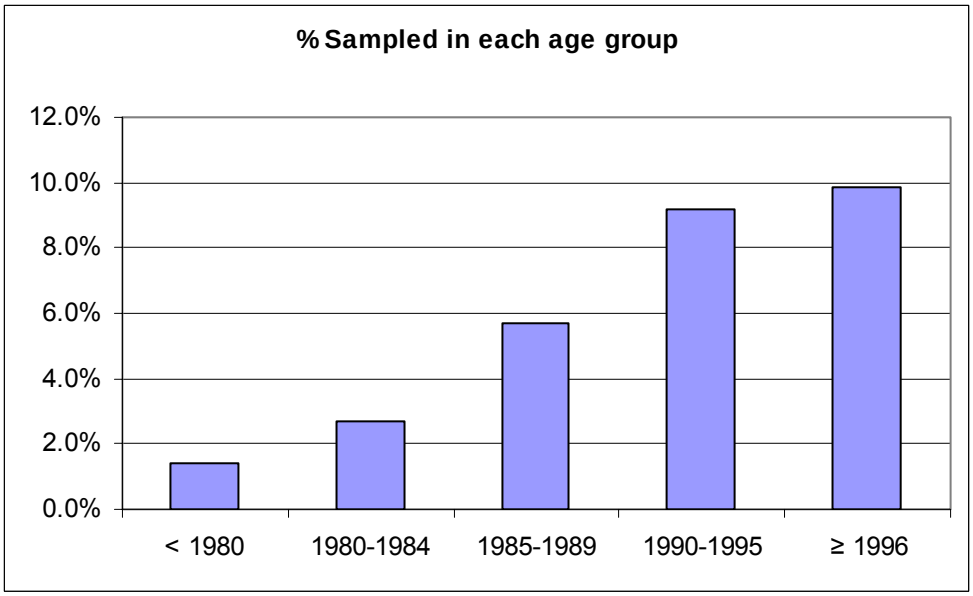

Figure 22. Surveyed vehicles grouped by vehicle year.

The data of exhaust emissions obtained from the surveyed cars were analyzed to see the percentage of cars in each vehicle year classification that would exceed the emission limits for carbon monoxide (CO), hydrocarbons (VOCs), and oxides of nitrogen (NO_x). Carbon dioxide (CO_2) was also monitored, but it is not reported here as it is not a presently regulated automobile emission pollutant. Each pollutant was evaluated

individually, which means that a single vehicle could potentially fail emissions testing based on one, two, or all three emission limits.

Figure 23 shows the percentage of vehicles by vehicle year that would fail an oxides of nitrogen emissions test, based on a concentration limit 1776 ppm. As seen in the figure, all of the age classes are below a 15% failure rate. This means that a low number of cars are failing for NO_x, which is the pollutant of concern for $PM_{2.5}$ formation. The percentage of vehicles that failed on the basis of NO_x is small compared to the results for CO and HC. Overall, 4.5% of the measured vehicles would presumably fail an inspection test, accounting for 25.4% of the total automobile NO_x emissions. The average tailpipe NO_x concentration measured was 396 ± 11 ppm.

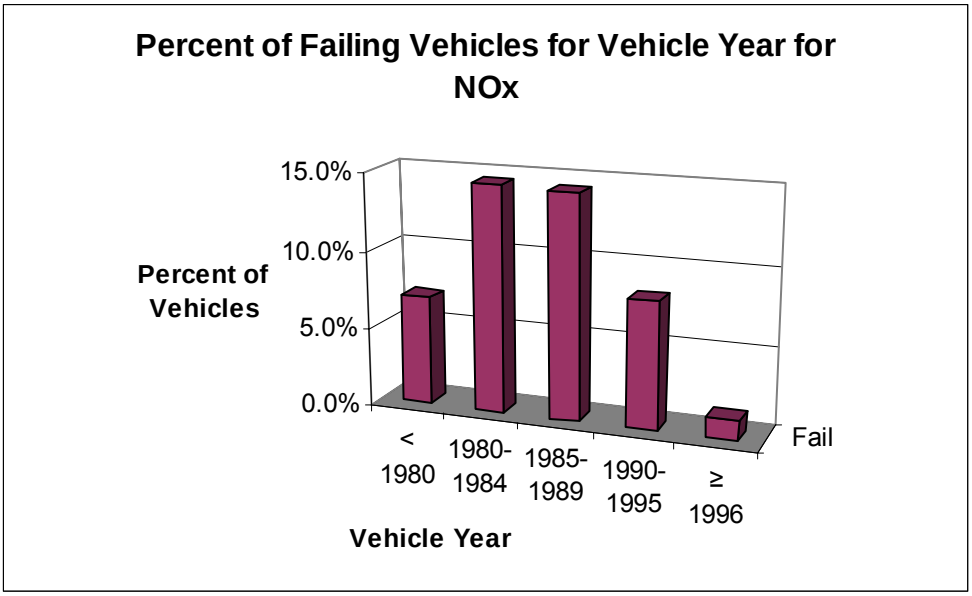

Figure 23. Percent of vehicles by vehicle year exceeding NO_x emission limits.

The older cars and newer cars result in a smaller percentage of failures than vehicles with a vehicle year of 1980 to 1989. It can be seen from Figure 24 that once again the average NO_x concentration for failing vehicles is not heavily dependent on vehicle year.

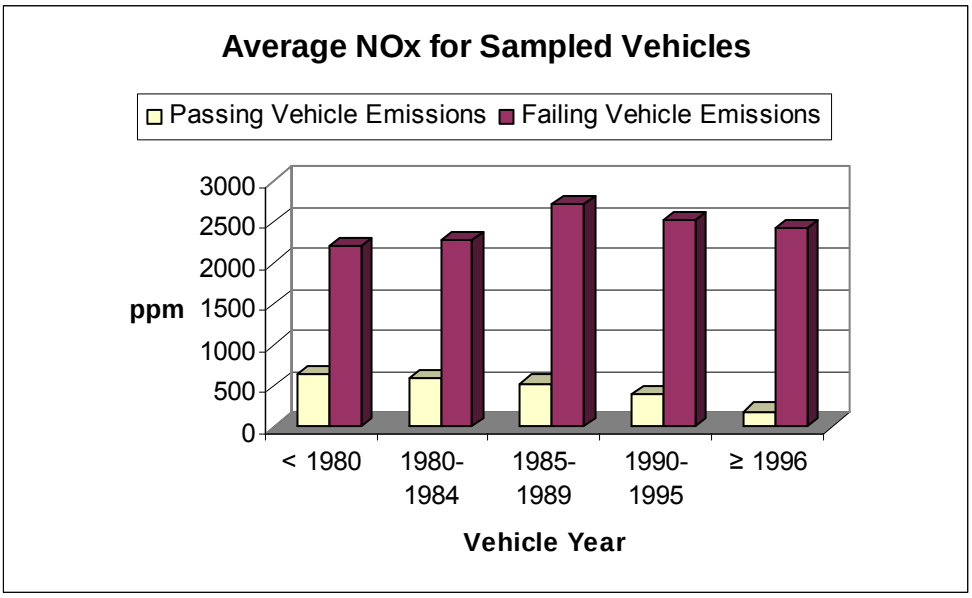

Figure 24. Average passing vehicle emissions versus average non-passing vehicle emissions for NO_x.

The data trends for hydrocarbons (VOCs) as shown in Figure 25 are similar to those of NO_x. Older vehicle year bins have a high percentage of emission failures, while newer vehicles have a smaller percentage of failures. The percent of failing vehicles for hydrocarbons is based on a failing limit of 225 ppm. The average tailpipe VOC concentration measured was 99.6 ± 14.2 ppm. Overall, 10.3% of the measured vehicles would presumably fail an inspection test, accounting for 47.8% of the total automobile NO_x emissions.

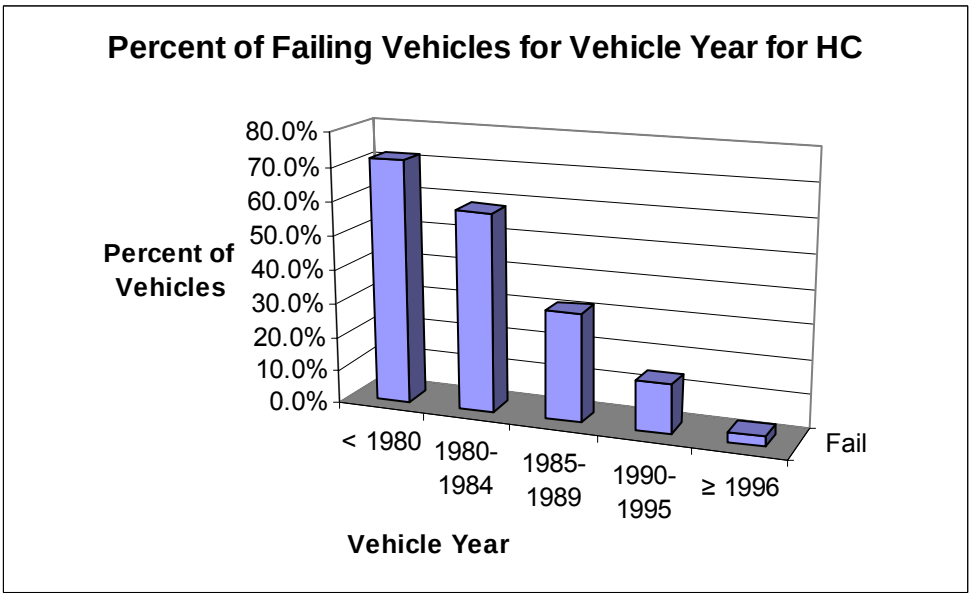

Figure 25. Percent of vehicles by vehicle year exceeding VOC (HC) emission limits.

From Figure 26, it can be seen that the failing vehicles emit on average 6 times more hydrocarbons than those that pass. Once again, the vehicle year does not have a big impact on the hydrocarbon concentration being emitted by the failing vehicles.

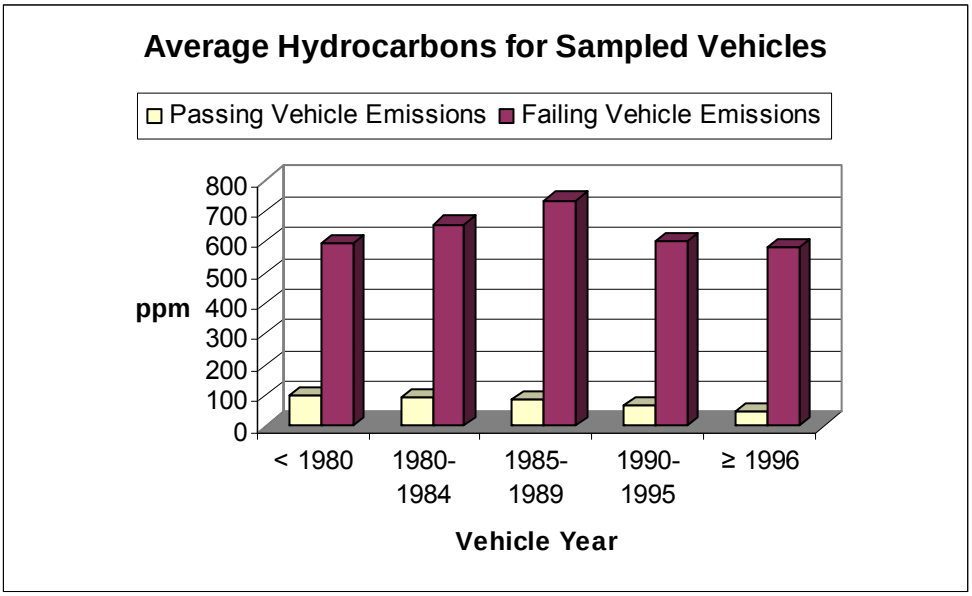

Figure 26. Average passing vehicle emissions versus average non-passing vehicle emissions for VOC (HC).

Although, not relevant to Cache Valley's $PM_{2.5}$ problem, nor a CO problem, it is interesting to examine the vehicle fleets CO emissions with respect to the number of "high" emitters. Overall, the average CO concentration was 0.61 ± 0.05% (at the 95% confidence interval). Figure 27 shows the percentage of vehicles sampled per vehicle year classification that would fail emissions test based on carbon monoxide with a limit of 1.14% CO. In total, 11.4% of the observed vehicle fleet would fail such an emissions test and these vehicles were responsible for 45.9% of the total measured CO. From Figure 27 it can also be seen that the highest percent of vehicles that would fail according to year are those that are older than 1985. It also shows that less than 10% of the vehicles that are newer than 1995 would fail an emissions test for CO.

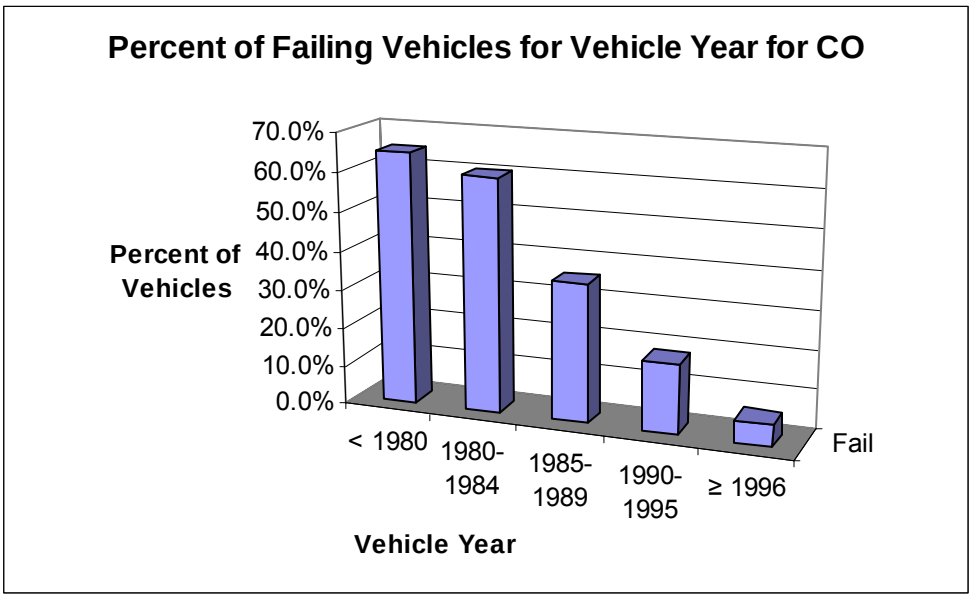

Figure 27. Percent of vehicles by vehicle year exceeding CO emission limits.

From Figure 28, it can be seen that the failing vehicles appear to emit on average of five to seven times more CO by percentage of total exhaust than the passing vehicles. It is important to note that the average CO concentration for the failing vehicles does not vary greatly with vehicle year. The 1996 and newer cars that would fail an emissions test are also significant emitters like the older cars.

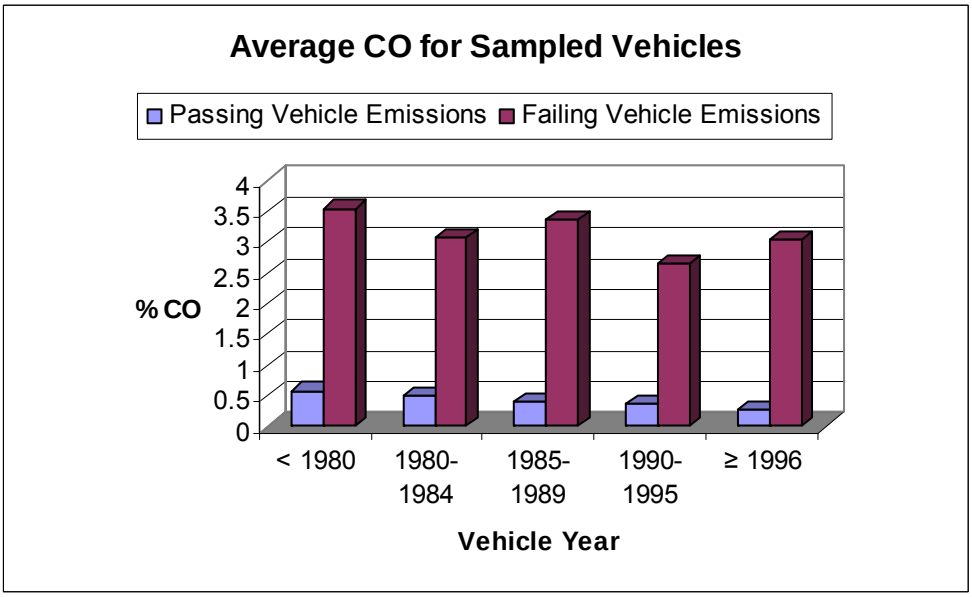

Figure 28. Average passing vehicle emissions versus average non-passing vehicle emissions for CO.

The percent of vehicles that would fail per age class for each pollutant was projected onto the Cache Valley fleet numbers and is shown in Figure 29. The greatest number of cars projected to fail emissions testing would do so because of CO emission violations, except in the vehicle year bin of 1980 and older, where more cars would fail due to VOC (HC) emission violations. The greatest number of potentially failed emissions tests would come from the vehicle bins 1985 through 1989 and 1990-1995. The percentages and totals of failing cars can not be summed because some of the vehicles would be counted more than once due to failing two or more emission tests.

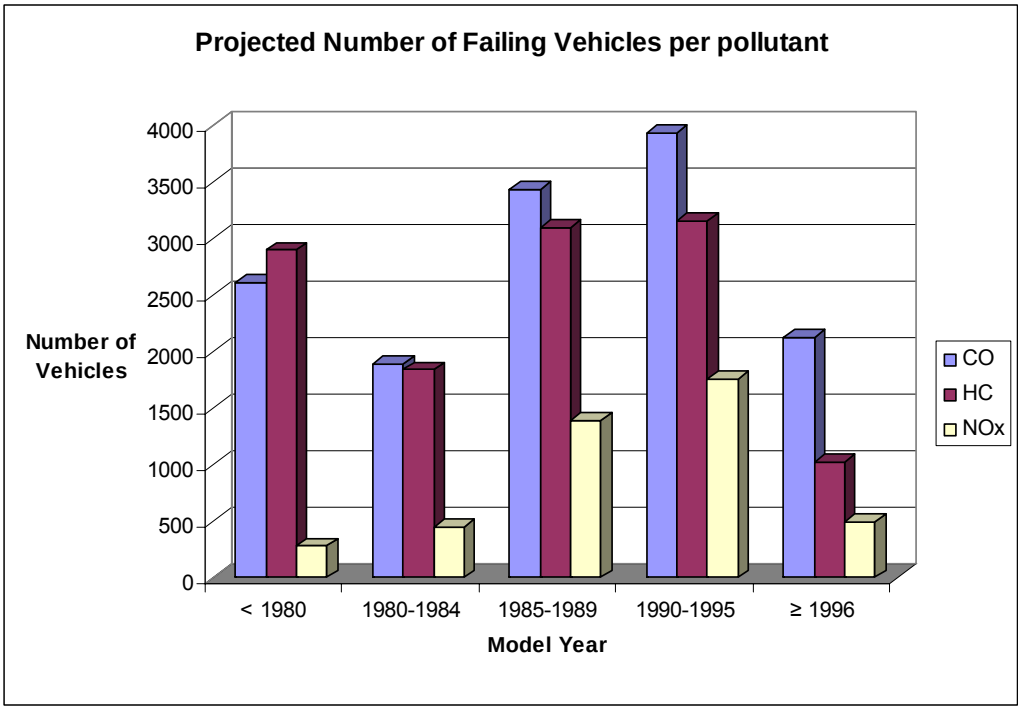

Figure 29. Projection of Cache County vehicles expected to fail emissions test based on CO, VOC (HC), and NO_x emission limits.

It is of interest to compare the average emission concentrations of the target pollutants from Cache Valley to a similar study conducted in Utah County during 2003. These results are shown in Figure 30. As can be seen, the average automobile emission concentrations for NO_x, VOCs (HC), and CO were all lower for the Cache County data set, even though an automobile I & M program is currently in place Utah County, but not Cache County. It should be noted from figure 30; however, that only the NOx emission concentrations showed a statistically significant difference (at the 95% confidence level). At this point, no explanation can be given for this apparent discrepancy. However, possible explanations could include differences in vehicle fleet structure, the possible inclusion of larger engine (pickup, SUV) vehicles in the Utah County study, or perhaps different test conditions (season, relative site locations, vehicle operating conditions).

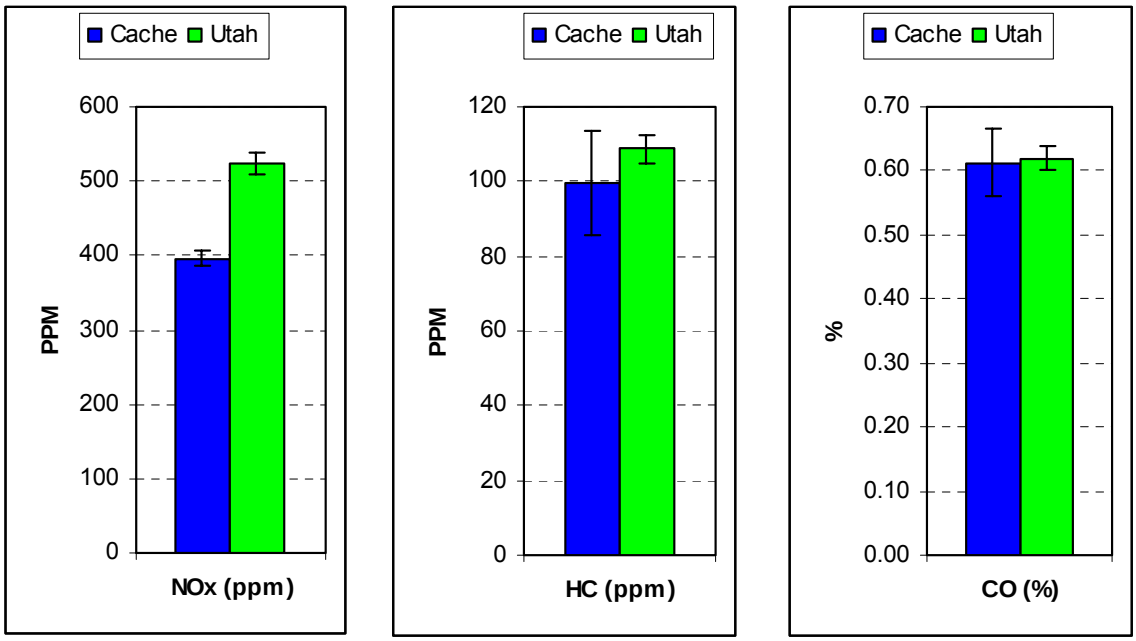

Figure 30. Average on-road vehicle emission concentration for Cache and Utah Counties.

The data that was obtained for the Cache Valley has been compared to similar data collected in Virginia in 2003. In order to compare the Cache Valley data to Virginia the vehicle specific power was calculated for each vehicle that was sampled. The pollutant concentration was then compared to the vehicle specific power to allow a common term in comparing pollutant concentrations. Virginia has an existing vehicle inspection and maintenance program, so by comparing the average pollutant concentrations per vehicle specific power one can obtain an approximation of the reductions in emitted pollutant concentrations from the vehicles.

Other researchers have suggested that a parameter referred to as vehicle specific power (VSP) may be a relevant way to relate vehicle emissions to engine operating conditions. VSP is defined as the vehicle's estimated engine power divided by the mass of the vehicle and is typically given in units of kilowatts per metric ton (kW/t). In practice, VSP can be found as using empirical relationship given by Klausmeier and McClintock (2003) as:

$$VSP = 4.364*\sin(\text{Grade in deg}/57.3)*\text{Speed} + 0.22*\text{Speed}*\text{Acceleration} + 0.0657*\text{Speed} + 0.000027*\text{Speed}^3$$

Klausmeier and McClintock (2003) reported for a Virginia study that NO_x emissions increase with VSP until a maximum occurred somewhere between 15 and 30 kW/t, depending on the age of the vehicles, with the older age vehicles reaching higher maximum NO_x emissions at lower VSP values. The Virginia hydrocarbon (VOCs) emission did not show as dramatic of variances with VSP; however, some decreasing

VOC emissions with increasing VSP were observed particularly for older (pre 1985) age class vehicles

Figure 31 shows the oxides of nitrogen emissions concentrations as compared to vehicle specific power for the different age classes observed in the Cache Valley study. The Cache Valley NO_x concentrations are generally greater (≈2x) for the given range of VSP than the Virginia data reported by Klausmeier and McClintock (2003), where a vehicle I & M program is in place. This may indicate that a vehicle I & M program would be beneficial in reducing the amount of NO_x emitted into the Cache Valley atmosphere by vehicles, but may also be caused by differences in vehicle fleet (although comparison to VSP and vehicle age should normalize that out.

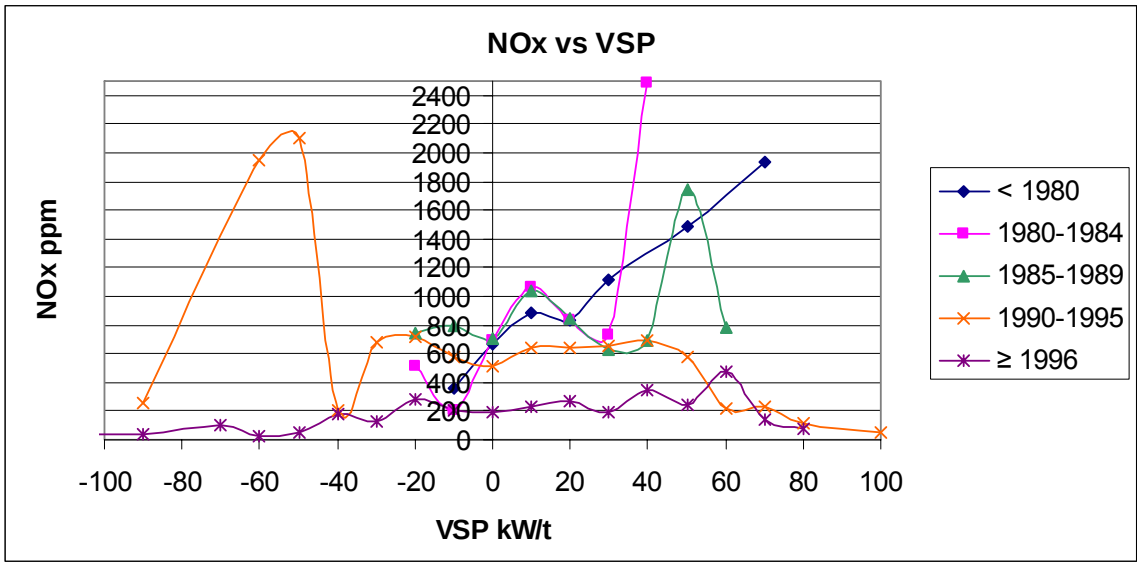

Figure 31. Cache Valley vehicle specific power compared to NO_x emission concentrations.

Figure 32 shows the hydrocarbon (VOC) emission concentrations as compared to vehicle specific power for the different vehicle age classes measured during the Cache Valley study. Comparing the data in Figure 32 to the previously mentioned Virginia data, it can be shown that the Cache Valley VOC concentrations are generally comparable to the Virginia hydrocarbon concentrations and both data sets show relatively little variation of VOC concentrations with VSP. This suggests that VOCs are not a strong function of the engines' workload, but rather a function of the engines' operating functions. an I/M program would not be very beneficial in hydrocarbon reduction.

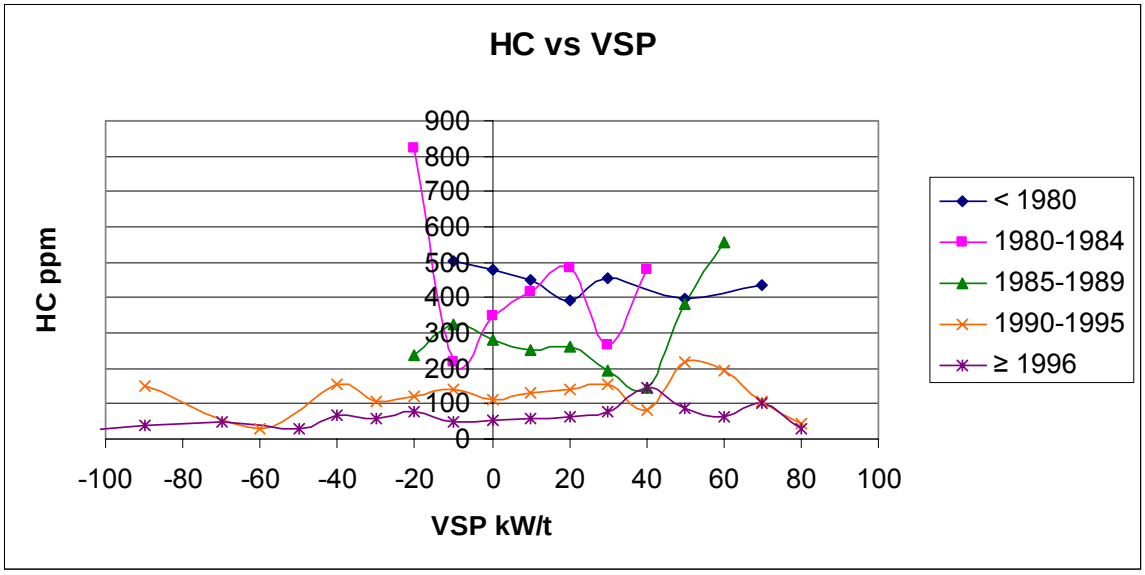

Figure 32. Cache Valley vehicle specific power compared to VOC emission concentrations.

ON-ROAD VEHICLE EMISSIONS STUDY CONCLUSIONS

From the information on registered vehicles that was obtained from the Utah Department of Motor Vehicles, the percentage of vehicles that are 1996 or newer was determined to be 49.4%. This means that approximately half of the registered cars in Cache Valley would be eligible for I & M testing with the OBD method.

The results of this study have also found that the majority of vehicles that would fail a vehicle inspection and maintenance test would do so for hydrocarbons (VOCs) and carbon monoxide (CO), although the latter is not presently of concern in the Cache Valley, and that the majority of the vehicles that would fail would be older than 1996. The study indicated that approximately 4.5% and 10.3% of the Valley's vehicles would fail inspections tests for NOx and VOCs, respectively, and that these vehicles were responsible for 25.4% and 47.8% of the valley-wide emissions. The study has also shown that the average pollutant concentration for failing vehicles does not vary greatly with vehicle year. The 1996 and newer vehicles that would fail an emissions test are significant pollutant contributors just like their older counterparts.

The comparison of the Cache Valley data to a similar study conducted in Virginia in an area with an I & M program suggests that the NO_x emission concentrations may be lowered with a local inspection program (based on the relationships between NO_x emissions and engine workload). A similar comparison with VOCs suggest an I & M program may not improve VOC emission rates.

CACHE VALLEY AIR QUALITY PHONE SURVEY

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INTRODUCTION

A random public phone survey was conducted in order to understand the feelings of the general public concerning the air quality and potential remediation scenarios within Cache Valley. The survey was conducted in the Fall of 2004 by undergraduate Environmental Engineering students. The students randomly selected names and numbers from the the Cache County phone directory and called the residents until a total of 100 hundred response were obtained. As a separate, comparative exercise, a similar survey was given to the students Fall 2004 class of USU's CEE 3610 (Environmental Management).

THE PHONE SURVEY

The citizen phone survey began with explanation of what the survey was for and queried the respondent as to if they would like to participate. If they agreed they were asked the following ten questions:

1) How severe is Cache Valley's air pollution problem (not a problem, small problem, medium problem, large problem, severe problem)?

2) Would you support a vehicle emission and inspection program (yes or no)?

3) How much would you be willing to pay for an I & M program (county should pay, $10-$20, $20-$30, or $30-$40)?

4) Do you think all of your cars would pass such a test (would pass, some would pass, would not pass)?

5) How many vehicle and licensed drivers are in your household?

6) What are you willing to do to reduce vehicle miles traveled (nothing, car pool, public transit, alternative transportation, trip consolidation, stay home) -- you may pick more than one?

7) What is your home's primary source of heating?

8) Are there any additional sources of heating in your home? If so, what are they?

9) Do you comply with Cache Valley's current "No-Burn" days (not applicable, never comply, mostly comply, always comply)?

10) Have you experienced a respiratory illness during Cache Valley's elevated pollution episodes (yes or no)?

The student survey questions asked for the number and year of cars, what county each car is registered in, and what could be considered a "reasonable" price for emission

inspections. The results from this survey may be more biased since all students have a somewhat similar background and "stage-of-life" status.

THE SURVEY RESULTS

The Residents Phone Survey

The phone survey showed Cache Valley's opinion and desires for solving the air quality problem. Figure 33 shows a fairly even spread of opinions concerning the severity of the problem. The combination of severe problem and large problem account up to 41% of the population compared to 32 % that believe there is no problem or a small problem.

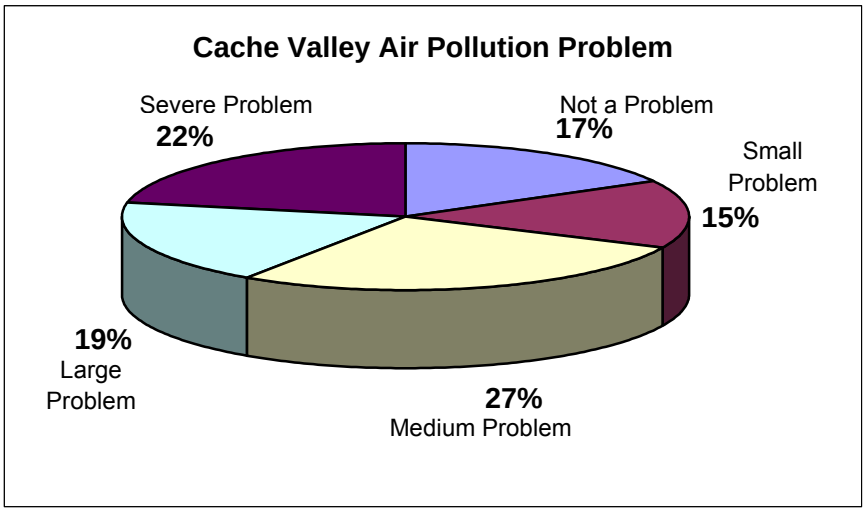

Figure 33. Q1: How severe is Cache Valley's air pollution problem?

Figures 33 and 34 illustrate the publics acceptance of an I & M program in Cache Valley and how much they would be willing to pay for it. Seventy four percent (74%) of the residents surveyed would support an I & M program and 54% would pay $10-$20, while 19% would pay $20-30$. It should be noticed that the percentage of people that would not support an I & M program (26%) is close to the percent of people who would prefer that the county tfund such a program (23%). This would likely indicate that those who would not support an I & M program, would prefer the county to pay for it. Figure 35 shows that most of the surveyed residents (82%) believed all of their vehicles would pass and I & M test, while only 2% believed there vehicles would fail.

Question 5 (How many vehicle and licensed drivers are in your household?) resulted in a ratio of 1.10 cars per licensed driver.

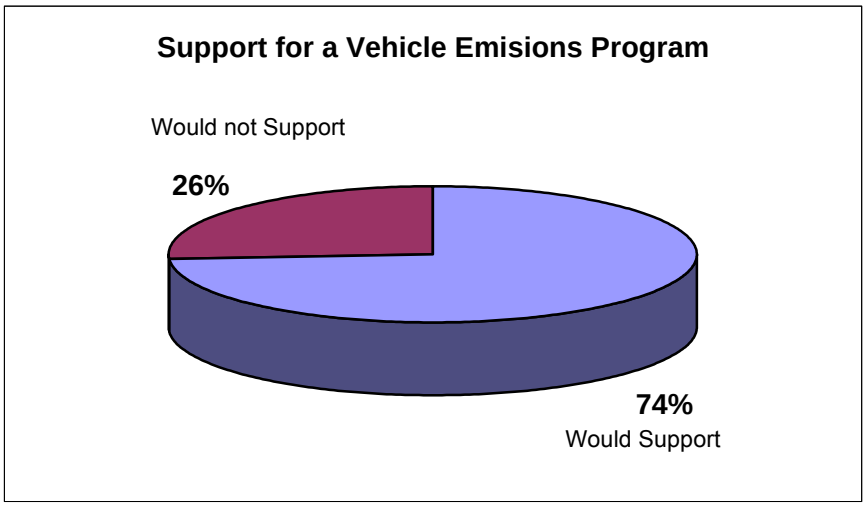

Figure 33. Q2: Would you support a vehicle emissions program?

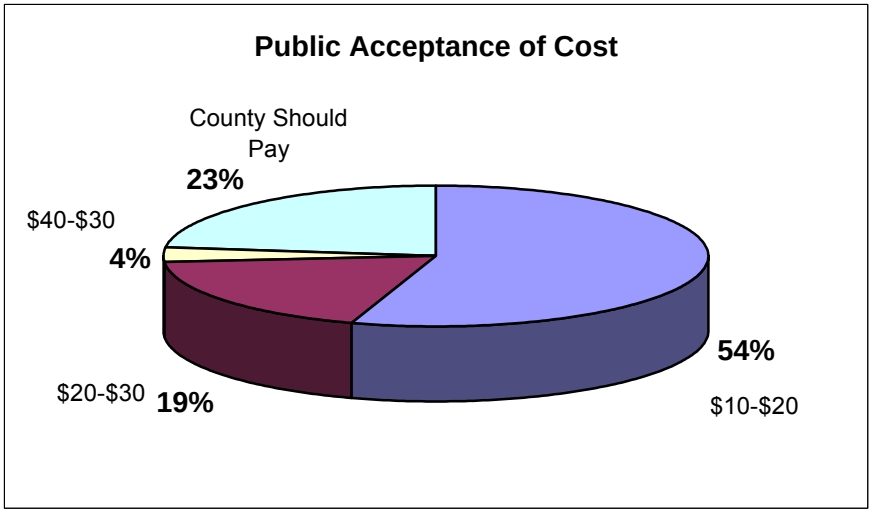

Figure 34. Q3: How much would you be willing to pay?

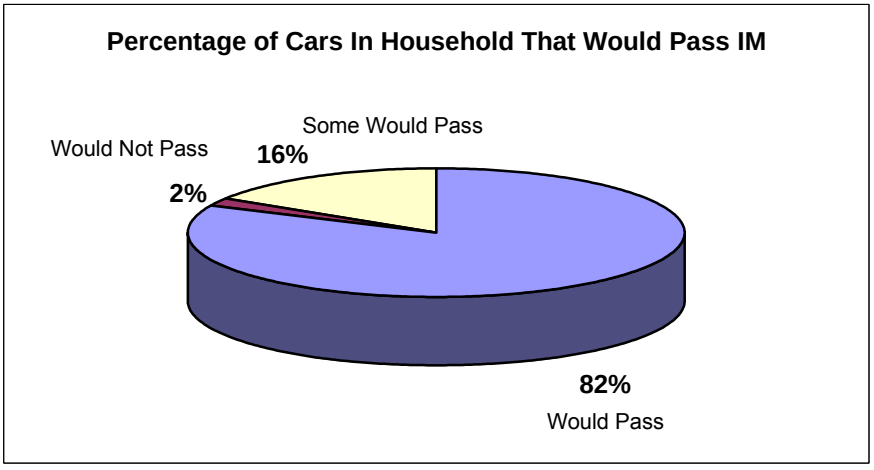

Figure 35. Q4: Do you think all of your cars would pass?

The public's acceptance of alternative ways to reduce Vehicle Miles Traveled (VMTs) was fairly evenly distributed between the presented options with only 5% of surveyed participants not willing to reduceVMTs (see Figure 36). This gives the County another option for increasing air quality in the valley by promoting items such as public and alternative transportation, and car pooling

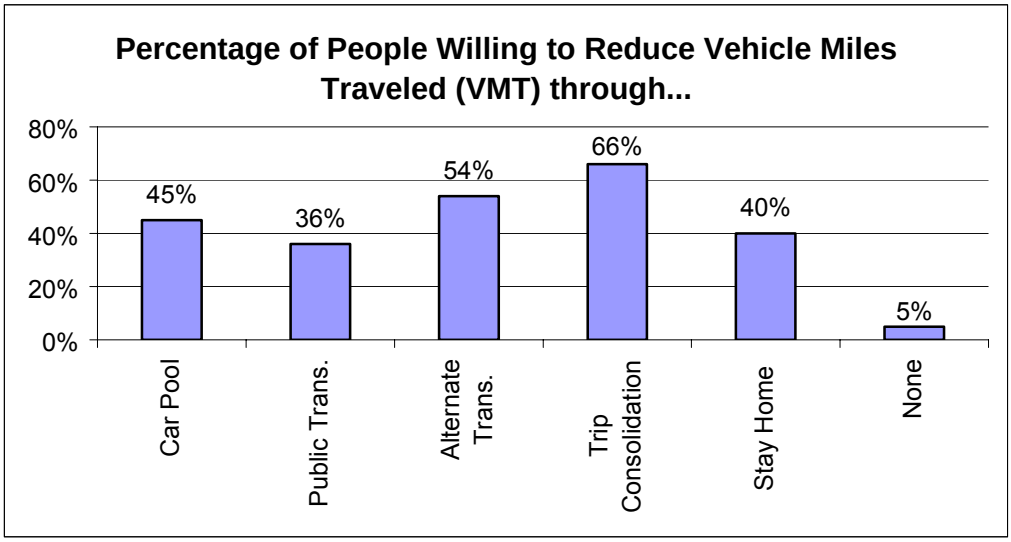

Figure 36. Q6: What are you willing to do to reduce VMTs?

Figures 37, 38 and 39 illustrate the public's means of heating their homes and compliance with county policies. Most all homes are primarily heated with a gas furnace (94%), while very few have a secondary source (total of 40%). Of the secondary sources, however, 27% were coal or wood burning stoves, the only heating source presenting a potential air quality problem. Of the all the people surveyed, 30% mostly complied with no burn policies, 11% always complied (59% were not applicable).

The final question asked if they had ever encountered any respiratory problems caused by the air quality in the valley and 11% of the people said they had (see Figure 40).

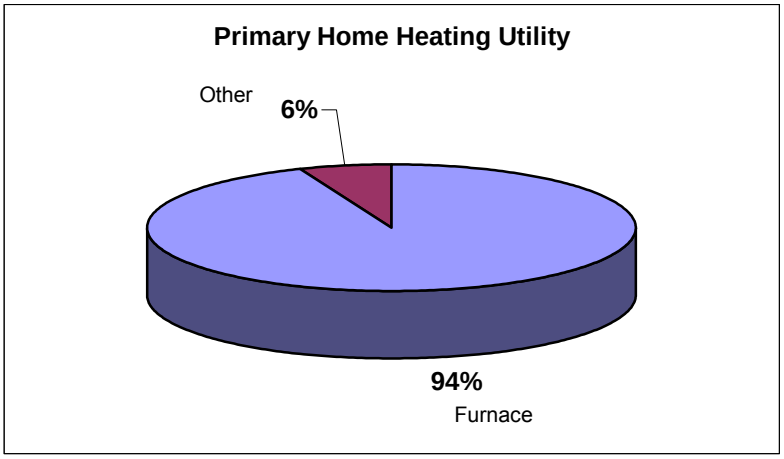

Figure 37. Q7: What is your home's primary source of heat?

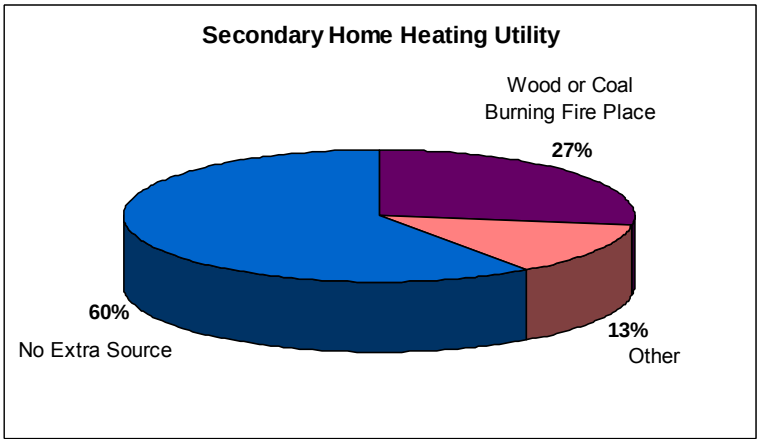

Figure 38. Q8: Are there any additional sources of heating in your home?

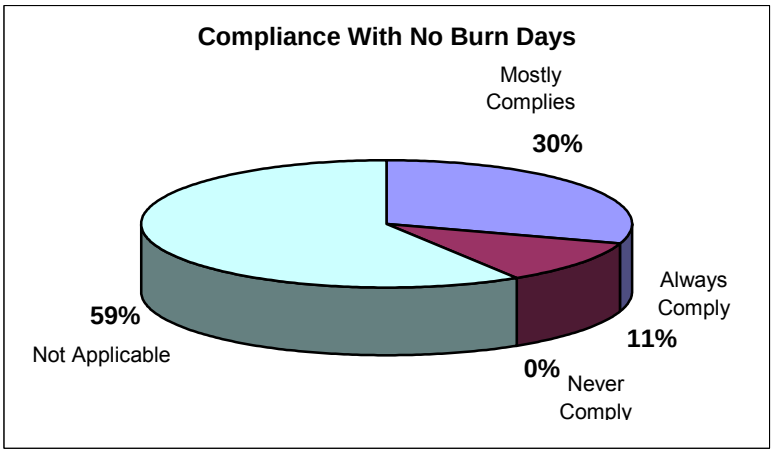

Figure 39. Q9: Do you comply with "no Burn" days?

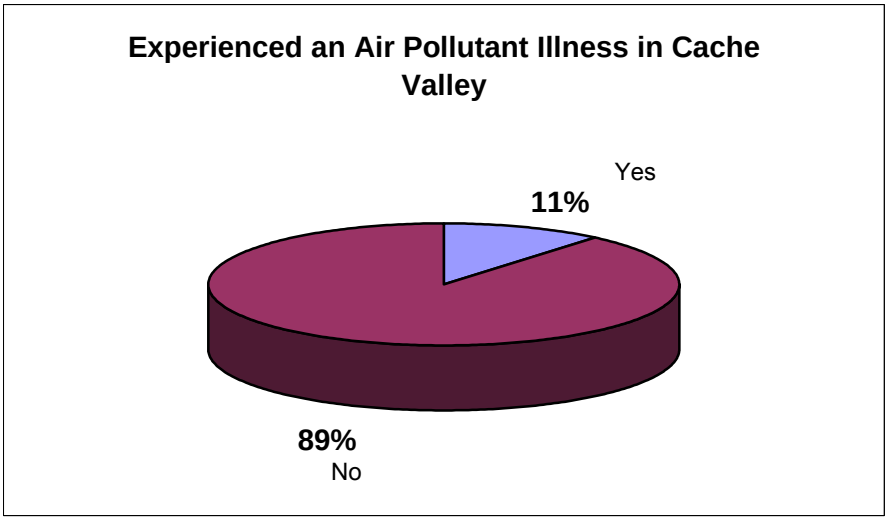

Figure 40: Q10: Have you ever experienced a respiratory illness during Cache Valley's elevated pollution episodes?

The Student Survey

The CEE 3610 Environmental Management class was surveyed with 79 students in attendance. The responses to the survey questions are shown in Figures 41 through 44. The average number of cars per student was calculated at 1.59, with one student responding that he/she did not own a car.

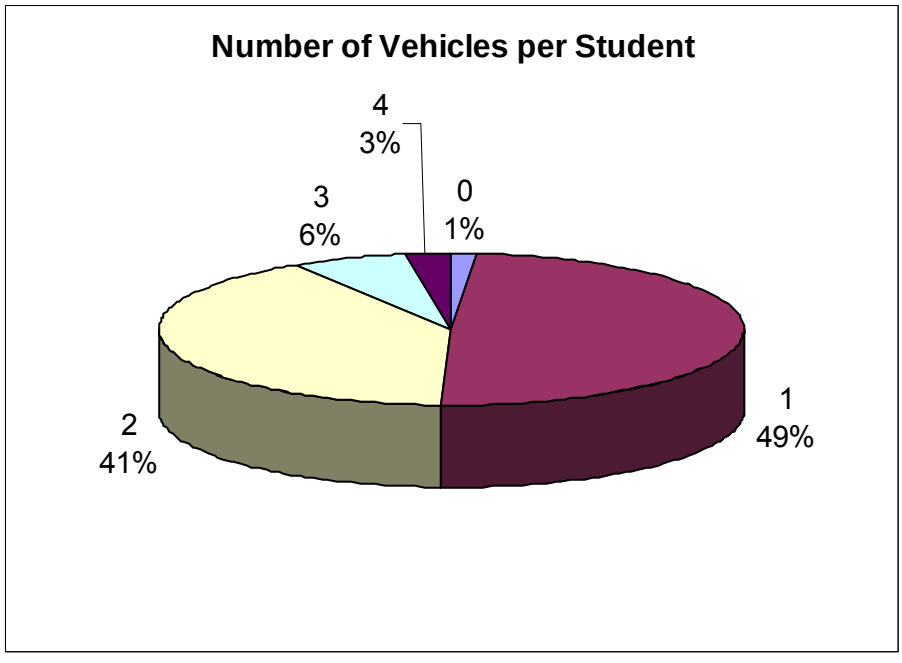

Figure 41. Number of vehicles per student (% of 79 students surveyed).

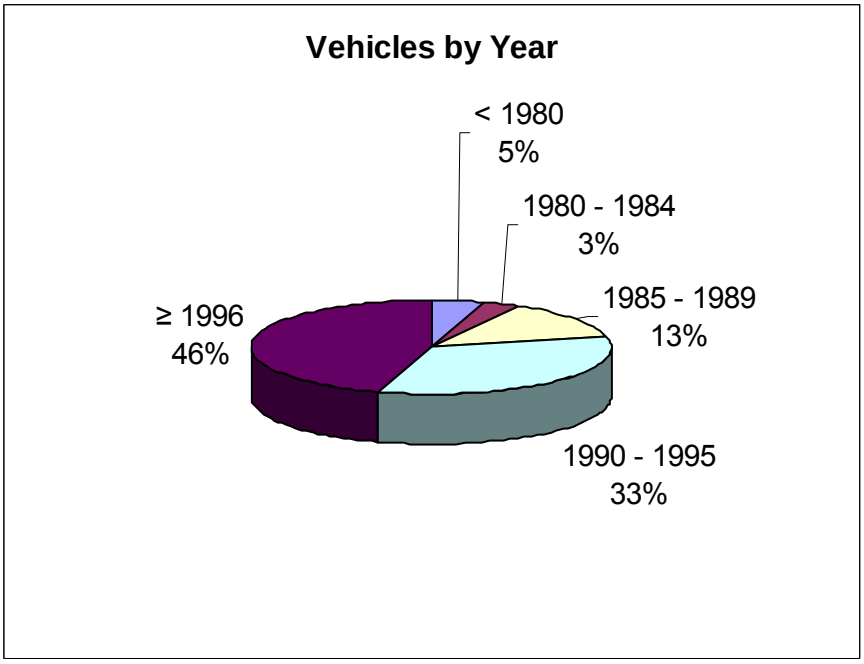

Figure 42. Student vehicles by age bin.

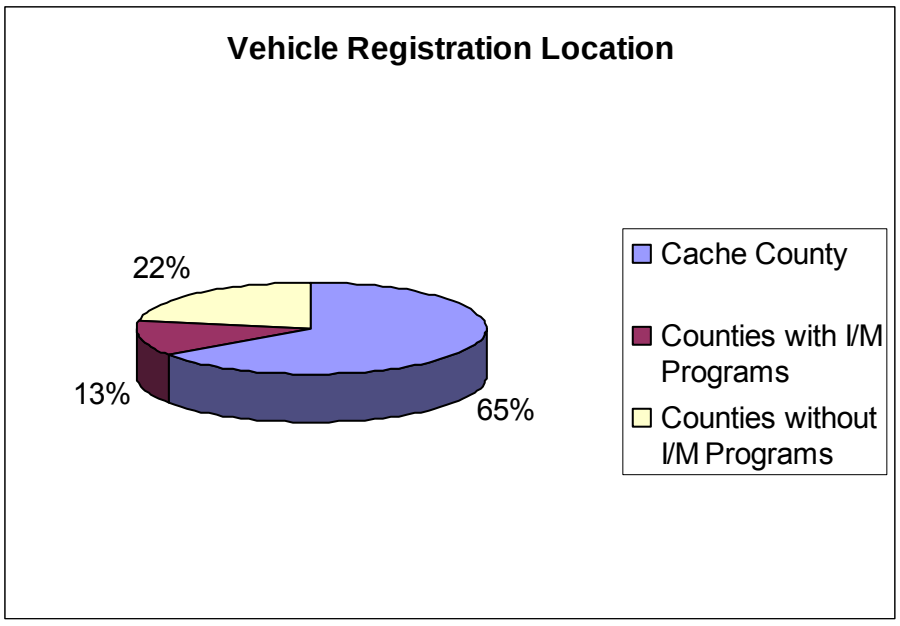

Figure 43. Student vehicle registration location.

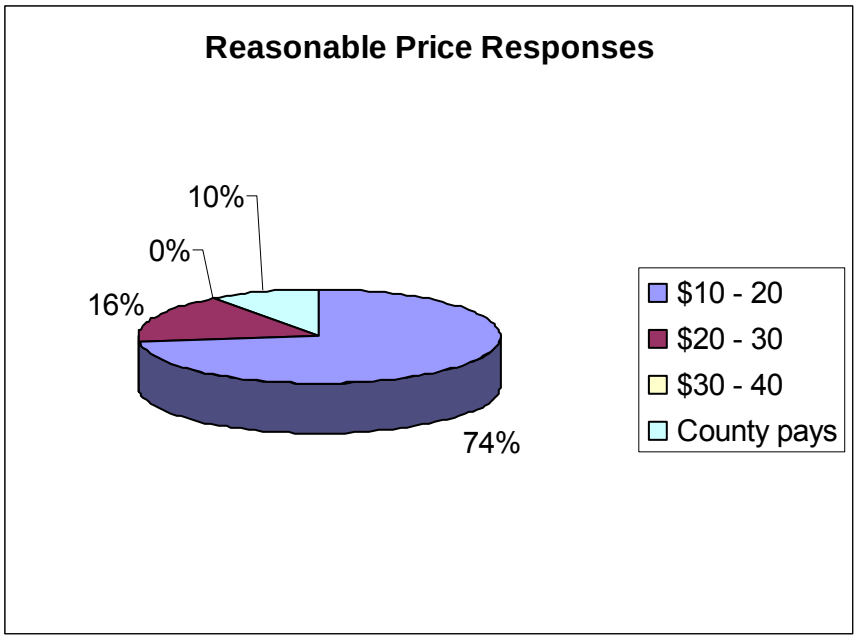

Figure 44. Student responses to reasonable I & M costs

The student survey results varied from public phone surveys in responses to cost for an I & M program. Seventy four percent (74%) of students agreed to pay $10-$20 for a program would be reasonable, while the public percentage was 54% (refer to Figure 34 and 44). This could possibly be due to the average student income is significantly lower than the public average.

The number of vehicles used per student (not vehicles per licensed driver) can be evaluated in that, the majority of students (49%) used only one car and the next largest category being two cars. This can be explained by the percentage of married and single students in USU's engineering program. It can likely be assumed that the percentage of students with two cars are married (vehicles/ driver = 1) and the single students have only one vehicle. The age of vehicle distribution between students and the general public are almost identical

SURVEY CONCLUSIONS

Based on the above survey, the Cache County residents believe a significant air quality problem exists in the Cache Valley (68%) and are in support of a vehicle inspection and maintenance programs (54%). Furthermore, they would be willing to pay $10-20 for this service (74%). The public is also willing to take other measures to cut down on vehicle miles traveled in order to cut down on vehicle pollution. These measures include trip consolidation (66%), alternate transportation (54%), and car pooling (45%).

VERTICAL TEMPERATURE PROFILE MEASUREMENT

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INTRODUCTION

In order to better understand the inversions that occur in Cache Valley, small HOBO® H1 temperature sensors/data loggers were deployed beginning in the spring of 2003 at selected elevations along an east-west transect from the valley floor up a steep mountainside to a point above the expected inversion heights. Through the use of the data loggers, the establishment, growth, and duration of inversions within Cache Valley were monitored over the period of one year. Data analysis shows the presence of low-level radiation inversions with diurnal and seasonal variations in the shape, steepness, and longevity of the vertical temperature profile. Comparison with measured $PM_{2.5}$ values has shown a strong correlation between the duration of a temperature inversion and the ambient $PM_{2.5}$ concentration.

Background

Cache Valley is part of the transition between the basin and range topography of Nevada and Utah and the mountainous topography of the Rocky Mountains. It has a total area of about 300 square miles. Cache Valley is bounded on the west, south, and east sides by mountains and by hills on the north. The valley floor has an average elevation of 4500' asl, and the surrounding mountains reach a height of 9900' asl. The surrounding topography essentially creates a protected pocket or bowl of Cache Valley.

In a normal vertical temperature profile of the atmosphere just above the earth's surface, temperature decreases with increasing altitude. In such conditions, turbulence and wind can readily mix a given pollutant throughout the vertical profile. A temperature inversion, on the other hand, is a positive change in temperature with increasing altitude, or can be defined as a layer of lighter, warmer air on top of a layer of more dense, colder air. The warm air essentially places a cap on the lower air, trapping below the colder air and any pollutants therein. If the inversion persists, the concentration of pollutants in the trapped layer of colder air increases as more pollutants are added (Masters, 1998).

An example of an inversion is shown in Figure 45, obtained by driving up a canyon adjacent (east) to Cache Valley. There is a strong temperature inversion at about 5000' asl for both sampling periods. Two important things to note are that the sampling dates occur during the winter and that they are two years apart, suggesting the 5000' asl mark is a common inversion depth. In Cache Valley, winter-time temperature inversions occur due to the reflection of the sun's energy by the snow, which allows the air above to warm up faster than the snow covered ground, thus creating a positive change in temperature with increasing altitude at a point above groundlevel. High pressure cells create extended periods of clear skies, and these clear skies combine with snow cover (high albedo) to produce strong temperature inversions over Cache Valley that can last for several days (see Figure 46). The surrounding topography contains the colder air trapped below, much like air trapped in a closed jar. Pollutants released within the valley become concentrated, often causing a haze. A low pressure front is required to break a persistent inversion, and the precipitation that sometimes follows clears the air of most of the particulate matter.

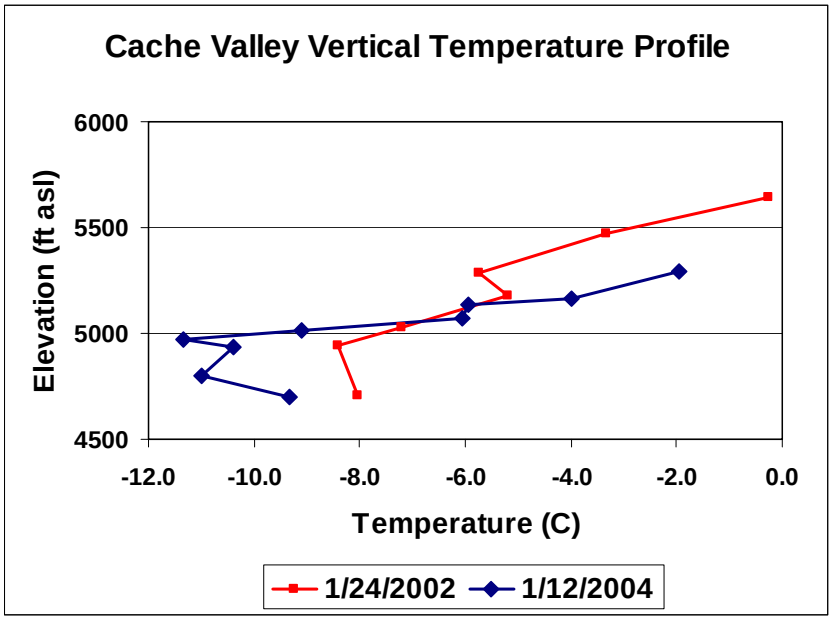

Figure 45. Temperature profile of Cache Valley obtained by driving up an adjacent canyon.

Figure 46. Cache Valley inversion as seen from an adjacent mountainside (ele. 6300' asl). The city of Logan, UT is faintly seen in the center.

METHODOLOGY

Typical measurements of temperature inversion heights, persistence, and growth are achieved through the periodic release of radiosondes or the use of a tethersonde (Arya, 1999). A radiosonde consists of a small, light-weight radio transmitter connected to temperature, pressure, and humidity sensors that are all attached to a helium-filled balloon. The balloon is released, and, as it ascends into the atmosphere, the radio

transmitter sends the measured data back to a receiver connected to a computer which interprets the data and stores it. A tethersonde differs from a radiosonde in that the balloon is attached to the ground via a tether. Sensor/transmitter systems may be dispersed along the tethering line, and may be used for longer periods of time than with a radiosonde. These methods provide very time-limited data, are time intensive, and require costly equipment. Other methods of obtaining inversion measurements include the use of acoustic and thermal adsorption techniques, which provide more time resolved data, but require complex and expensive equipment and can be time-intensive.

There are currently several commercially available temperature sensors/data loggers that have been developed for both scientific and commercial uses (Whiteman *et al.*, 2000). One such data logger, the HOBO® H1 (Figure 47) developed by Onset Computer of Bourne, MA, is a small, inexpensive unit consisting of a circuit board in a plastic case; waterproof cases are available for protection from water and sunlight. A similar product of Onset Computer, the HOBO® H8 Pro was found to be effective and accurate for meteorological applications by Whiteman *et al.* (2000). These systems require minimal attention and have a user-friendly software program. The HOBO® H1 data loggers were used to measure temperature inversion characteristics in Cache Valley.

Figure 47. HOBO® H1 temperature sensor/data logger and protective case.

Nine HOBO® H1 temperature sensor/data loggers were utilized to record ambient temperatures at separate locations and elevations. The sensors/data loggers were first calibrated to one another through the use of four co-located sampling periods. Derived calibration equations were used to adjust each respective data set. Since the data collected were only compared to one another to obtain relative temperature differences and not to obtain the actual temperature, it was not necessary to calibrate the sensors/data loggers with a Hg-thermometer. The sensors measured the temperature on a continuous basis, and the hourly average temperature was stored as a data point. The data were collected every six to eight weeks. The temperature sensors within the protective case were placed 2-3 meters above ground and in open areas to minimize terrestrial heating and ensure ventilation, respectively. The elevation of each sensor was based upon site accessibility and vertical spacing, and the final elevations are as follows: 4562', 4646', 4865', 5024', 5338', 5513', 5735', 6287', and 6576'.

RESULTS

The HOBO® H1 temperature sensors/data loggers obtained reliable data that were used to determine the characteristics of temperature inversions in Cache Valley. As a whole, they adequately measured the actual ambient temperature when compared with available, nearby meteorological stations.

The use of vertical temperature profiles averaged over a period of weeks or a month provides a good indication of the existence and characteristics of inversions, as can be seen by the average values for March 2003 in Figure 48. At 6:00 AM, just before the sun rises, there is a strong temperature inversion between about 4500' and 5400', but above that the temperature profile looks normal, except a possible existence of an upper level inversion at 6300'. After the sun rises, the valley floor begins to warm up, and by 9:00 AM the inversion is almost gone. As the day progresses, the valley increases in temperature and at about 3:00 PM the temperature profile almost mirrors the dry adiabatic lapse rate shown by the black dotted line. As the sun sets, the valley cools at a much faster rate than the air mass above, causing a temperature inversion to begin forming again before midnight. The cooling continues through the night as the diurnal evolution of the temperature profile comes to an end, completing the daily cycle. Also, note the broad range of temperature values over the entire profile. Similar results were produced through the analysis of data for spring, summer, and fall months.

On the other hand, if the averaged temperatures for the first half of January 2004 are examined, it is apparent that the temperature inversion doesn't form and break up each day, rather it is more diurnally consistent (Figure 49). Only during the warmest times of the day is the inversion seemingly affected by the surface warming. The range of temperatures throughout the vertical profile is also much smaller than that of March 2003, especially at higher elevations. This would suggest that winter months have more persistent inversions, as the first of January 2004 demonstrates.

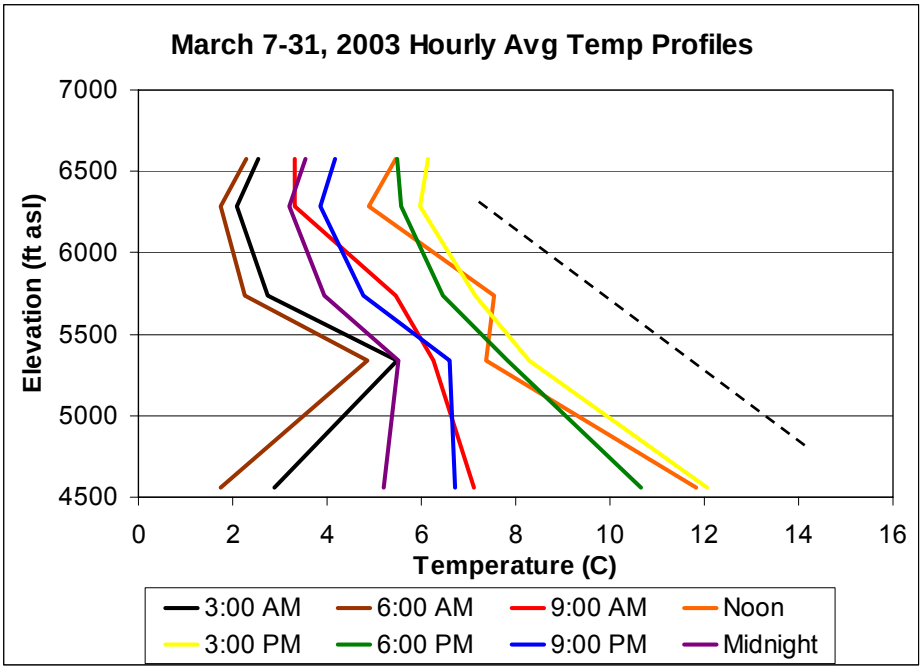

Figure 48. Average vertical temperature profile of Cache Valley for March 7-31, 2003.

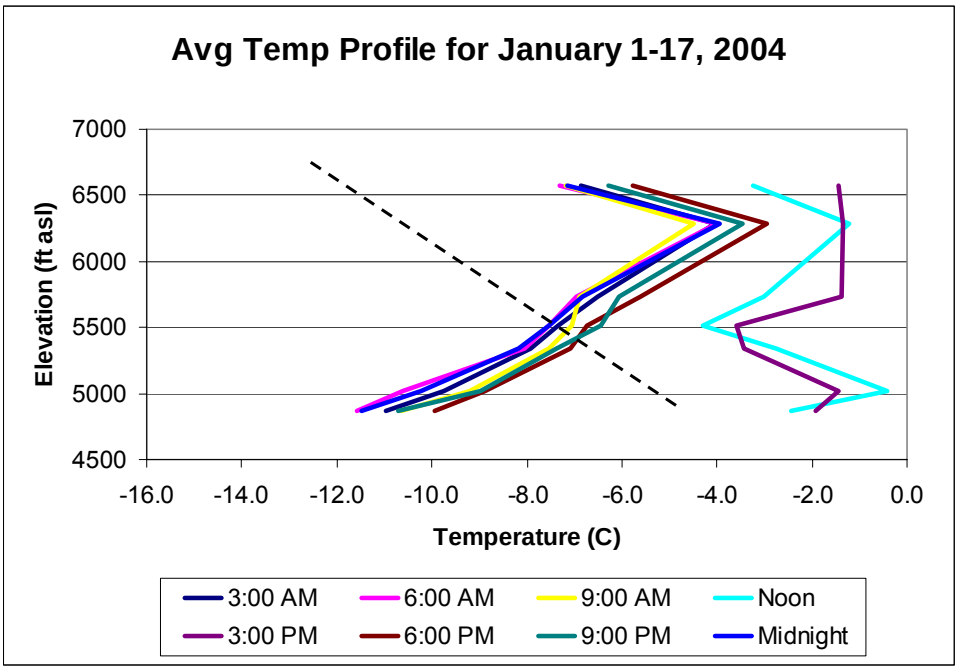

Figure 49. Vertical temperature profile over Cache Valley for January 1-17, 2004.

The data collected from the HOBO® sensors also proved very useful in examining the day to day changes in the temperature inversion. This day to day change can be seen for the month of January 2004 in Figure 50, with red representing warm temperatures, getting brighter as the temperatures grow warmer, and blue representing cold temperatures, growing brighter as the temperature decreases. It should be noted that the value of 2 is the first number on the x-axis, but it really represents midnight between January 1st and 2nd; there is not a day 32, instead it is midnight of the 31st. Early in January, data from the lowest sensor were not available, causing the blue patch on the bottom until the 18th.

From Figure 50, it can be seen that during the first couple of days of January 2004, it was fairly warm and no inversion was observed, or the cold air was above the warm air. However, the air temperatures dropped over several days and on about the 6th a temperature inversion began to appear, with warmer air above cooler air. As time progressed, the temperature difference between the air masses above and below increased, causing the temperature inversion to strengthen and become deeper. Just after the middle of the month, a couple of weak low pressure cells passed through the region, decreasing the temperature difference, but not completely breaking up the Cache Valley inversion. The inversion began building after each frontal system on the 18th and the 23rd. At the end of the month, a strong low pressure cell, with an accompanying snow storm, moved in to break up the inversion and provide some relief from the 20-day capping lid sitting over Cache Valley. The temperature profile returned to normal with cooler air above and warmer air below.

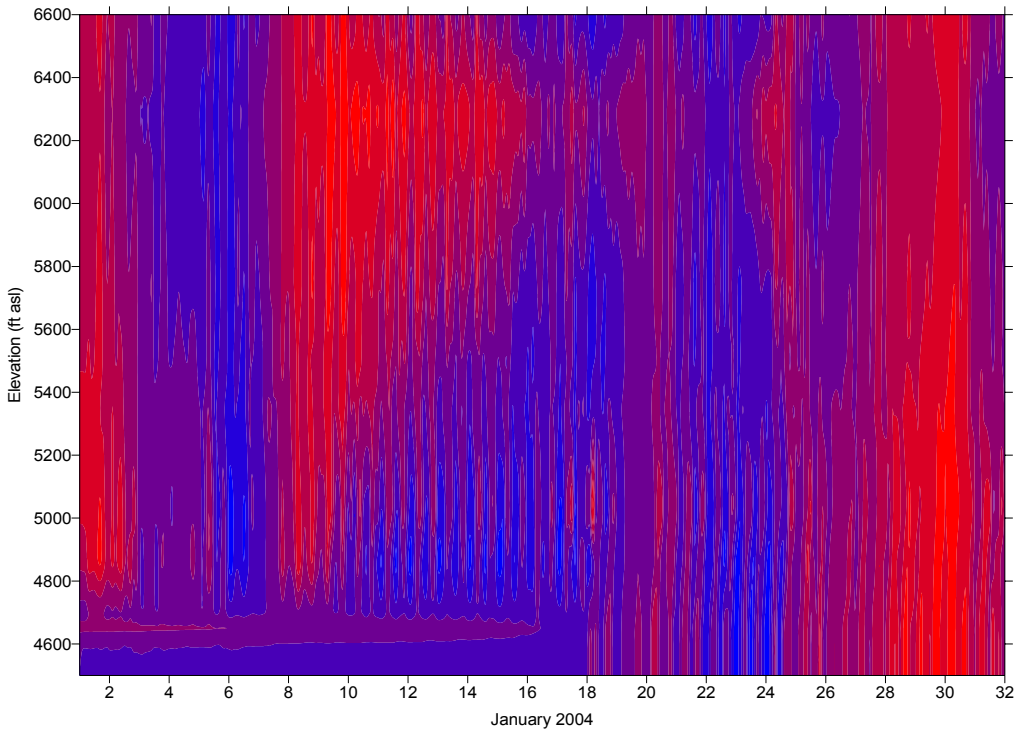

Figure 50. Temperature contour map of the air above Cache Valley with respect to elevation and time for the month of January 2004.

The temperature contour map clearly shows the growth and persistence of the inversion layer. To examine the affects of an inversion on the pollution concentration, the $PM_{2.5}$ concentrations for the month of January 2004 were overlaid on the temperature contour map in Figure 51. The solid yellow line represents the ambient $PM_{2.5}$ concentration as measured at the Logan city sampling location and the dotted green line represents the National Ambient Air Quality Standard (65 $\mu g/m^3$). The concentration of ambient $PM_{2.5}$ began fairly low, but as the temperature inversion started and strengthened, the concentration reached values double the national standard. Concentrations dropped when the inversion layer begins to break up due to the two weak low pressure systems, but continued to increase after each system passed. It was not until the strong low pressure system passed through at the end of the month that the $PM_{2.5}$ concentrations dropped below the NAAQS.

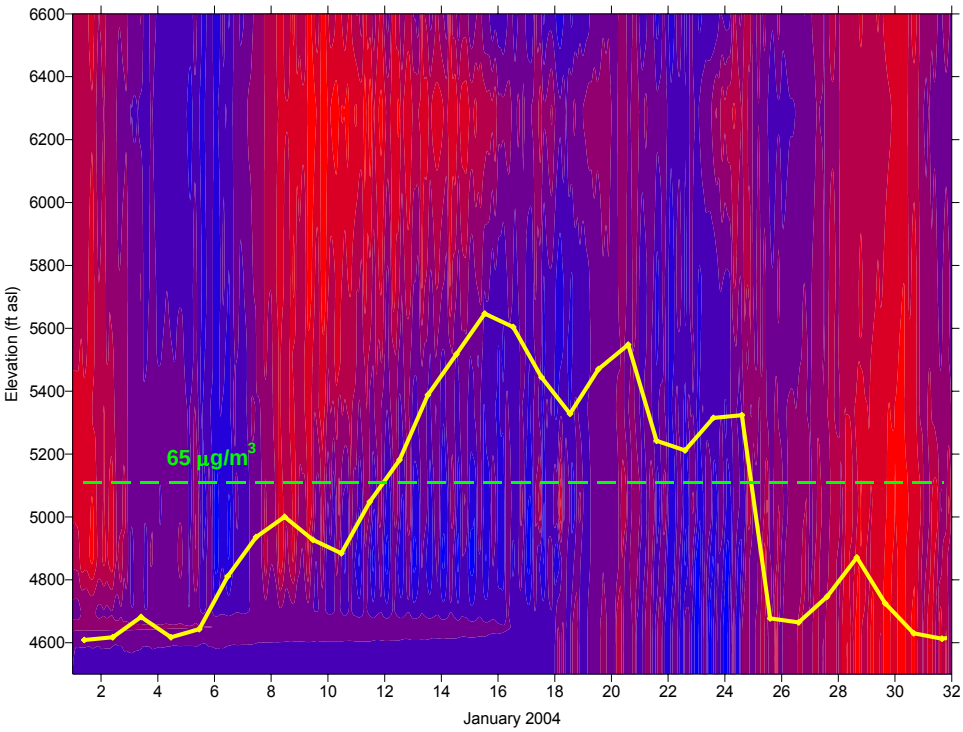

Figure 51. January 2004 temperature contour map with $PM_{2.5}$ concentration (yellow) and National Ambient Air Quality Standard (green).

CONCLUSIONS

The HOBO® H1 temperature sensors/data loggers were able to distinguish differences in the Cache Valley vertical temperature profile, including the evolution of temperature inversions. Despite being ground-based, the sensors/data loggers were sensitive and accurate enough to produce reliable data. Through data analysis, it was been found that diurnally fluctuating inversions dominate the vertical temperature profile for all but the colder months of winter, such as December, January, and February. The sensors/data loggers proved extremely useful in understanding the evolution of persistent inversions that occur in Cache Valley, as well as clearly demonstrating their effects on ambient $PM_{2.5}$ concentrations. This understanding will allow for better prediction of high pollution events and, therefore, aid in current and future pollution prevention efforts.

INDOOR/OUTDOOR PARTICULATE MATTER IN THE CACHE VALLEY

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INTRODUCTION

The health concern for $PM_{2.5}$ is because the particles are small enough to be breathed into the deep lung tissue and become deposited. Larger particles are filtered out in the nose and throat. The affects of the deposited particles depend on particle composition, dose, and the current health status of the individual. Daily (24-hr) averaged $PM_{2.5}$ levels as high as 133 and 138 $\mu g/m^3$ in the Cache Valley have been recorded during prolonged wintertime temperature inversions. Such high levels are strictly a winter-time problem for Cache Valley, as can be seen in Figure 52. During the spring, summer, and fall, the average is around 10 $\mu g/m^3$. As previously discussed in earlier sections, chemical analysis of the $PM_{2.5}$ in Cache Valley has shown that it is dominated by ammonium salts, which contribute 60-90% of the total particle mass, and that ammonium nitrate (NH_4NO_3) is the largest fraction by mass (Martin and Zhu, 2004; UDAQ, 2006). Ammonium salts are secondary pollutants as they form in the atmosphere through photochemical reactions, such as is generalized in the following:

$$NH_3\ (g) + HNO_3\ (g) \leftrightarrow NH_4NO_3\ (s) \qquad \text{(Equation 1)}$$

As this is an equilibrium reaction, temperature greatly affects the formation, or dissociation, of ammonium nitrate, causing a difference in K_{eq} values of greater than two orders of magnitude between 0 and 20ºC. Solid particles are favored at cold temperatures and gases are favored at warm temperatures (Seinfeld and Pandis, 1998).

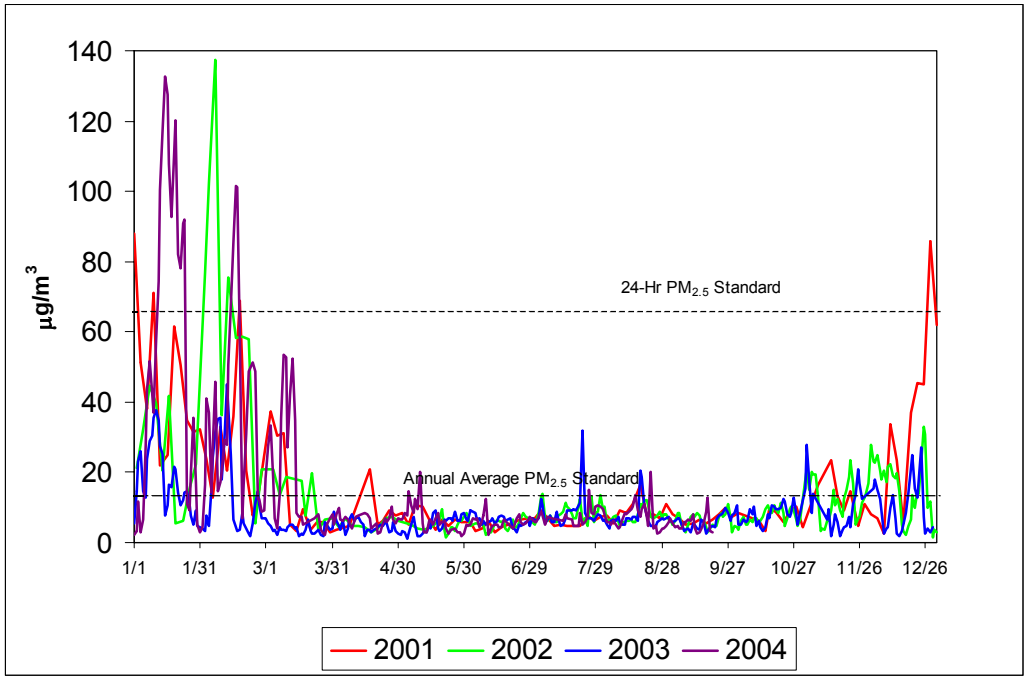

Figure 52. Cache Valley $PM_{2.5}$ concentrations as recorded for 2001-2004.

The average adult begins to feel the health affects of $PM_{2.5}$ at 65 $\mu g/m^3$, but those with compromised immune systems such as children, the elderly, and the ill may have noticeable affects at 40 $\mu g/m^3$. The Bear River Health Department (BRHD), in conjunction with the Utah Department of Air Quality (DAQ), has developed a public notice system to alert citizens of Cache Valley of the current air quality during winter months using the following color scale: "green" – good air quality, continue activities as normal; "yellow" – poor air quality, reduce vehicle mileage and those with compromised immune systems are recommended to remain indoors; "red" – bad air quality, reduce vehicle mileage and everyone is recommended to remain indoors. The $PM_{2.5}$ concentrations that divide green and yellow and yellow and red are 40 and 65 $\mu g/m^3$, respectively. The BRHD also suggests that school children remain inside during recess and lunch time on red days. However, the quality of the indoor air, with respect to $PM_{2.5}$, in comparison to the ambient air quality in the area schools was unknown. Therefore, it was also unknown if it was actually better to keep the children inside on high pollution days. This study was designed to determine the indoor air quality and answer the question as to whether it is best to keep the children inside or not.

Past research on indoor air quality versus outdoor air quality has shown that indoor $PM_{2.5}$ is usually less than outside, ambient levels. Sawant *et al*. (2004) found that indoor:outdoor ratios of $PM_{2.5}$ concentrations in schools in Mira Loma, CA during the fall of 2001 and winter of 2001-2002 averaged 38%. Chemical analysis further showed that the highest portion of $PM_{2.5}$ was organic carbon and that the indoor:outdoor ratio of nitrate was the smallest of all the chemical species (Sawant *et al.*, 2004). El-Abssawy (2003) confirmed that indoor particle concentrations were dependent on outdoor particle concentrations, indoor activities, and on particle size.

Based on these past studies and owing to the dominance of ammonium nitrate in the local $PM_{2.5}$, it was expected that local $PM_{2.5}$ concentrations would be lower indoor as compared to outdoor. Therefore, a study was initiated to examine any such differences.

METHODOLOGY

Three elementary schools and one high school in Cache Valley were chosen as sampling sites. Filter-based sampling was conducted using 0.45 µm Teflon filters with AirMetrics MiniVol impaction samplers. Paired samplers were placed both inside and outside of each school, as seen in Figure 53, and operated at simultaneous times to obtain comparable data. Sample times were during school hours, Monday through Friday from 8:00 AM to 4:00 PM local time and were collected over two to four day periods. Table 2 lists the school name, the location of both samplers, and the sampling dates. The UDAQ sampling site is located one block from Logan High School. The filters were analyzed for mass by comparing average pre-weights and post-weights. Anion chromatography was performed on solutions of the collected particles for nitrate (NO_3^-), sulfate (SO_4^-), nitrite (NO_2^-), and chloride (Cl^-).

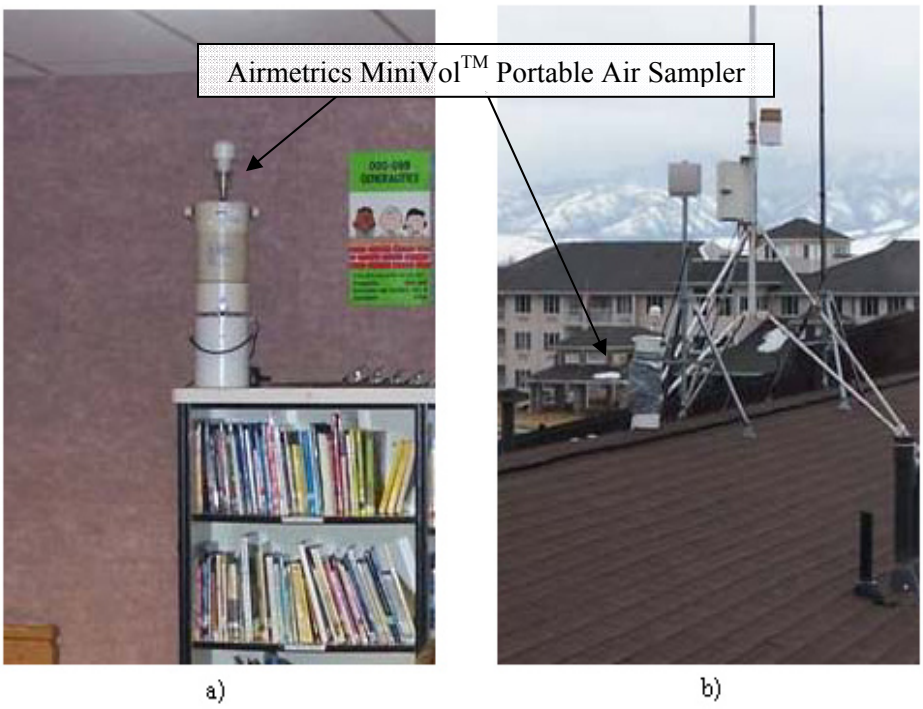

Figure 53. $PM_{2.5}$ samplers at Greenville Elementary a) in the library and b) on the roof.

School	Sample Dates	Sampler	Location
Greenville Elementary	Jan. 24, 2005 – Feb. 18, 2005	Inside	Library
		Outside	Roof
Summit Elementary	Jan. 11, 2005 – Feb. 11, 2005	Inside	Library
		Outside	Roof
Sunrise Elementary	Jan. 11, 2005 – Feb. 8, 2005	Inside	Library
		Outside	Roof
Logan High School	Feb. 9, 2005 – Feb. 25, 2005	Inside	Classroom
		Outside	UDAQ Sampling Site

Table 2. Sampling locations and dates by school.

RESULTS AND DISCUSSION

The results of the mass concentration analysis from both the indoor and outdoor samplers for each school are shown in Figure 54. The linear fit and R^2 value for each data set are also shown. Examination of the data show that while outdoor $PM_{2.5}$

levels nearly reached the 24-hr NAAQS of 65 µg/m^3, the indoor concentration at each of the four schools was well below the 40 µg/m^3 at which sensitive populations are suspected to be affected. In the data for Logan High School, one apparent outlying value caused a low R^2 value, but the data are otherwise well grouped. Without the outlier, an R^2 value of 0.5747 would be produced. The low slope values in the linear fit equations suggest that the indoor $PM_{2.5}$ is slightly affected by the outside concentration, but that most of the $PM_{2.5}$ is apparently removed.

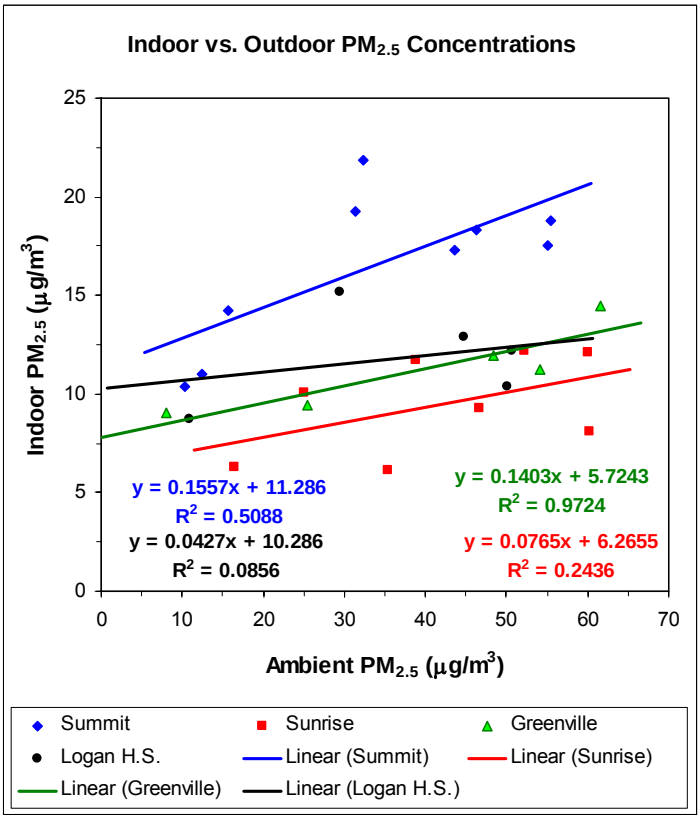

Figure 54. Indoor air quality versus outdoor air quality for all four schools.

The average measured ambient and indoor $PM_{2.5}$ concentrations are shown in Figure 55, along with the ratio of the indoor levels to the outdoor levels as a percent. The error bars show the 95% confidence intervals for each average value. The average outdoor concentrations for each school were not found to be statistically different from one another. The high variability seen in the outdoor values is expected due to changes in ambient temperatures and in the vertical mixing ability of the ground-level air mass caused by vertical temperature inversions, and by deposition of the particles during precipitation events. The indoor $PM_{2.5}$ concentrations are fairly constant as demonstrated by the low variability. Sunrise Elementary, Greenville Elementary, and Logan High School indoor averages were statistically the same, but Summit Elementary had a

statistically significant higher average concentration than the other three. Summit Elementary also had the highest average indoor:outdoor concentration ratio at 61.2%. This, however, was not statistically different than the average for both Greenville Elementary and Logan High School. The average indoor:outdoor concentration ratio for Sunrise Elementary was not statistically different than the averages for Greenville Elementary and Logan High School, but was significantly different from the average of Summit Elementary.

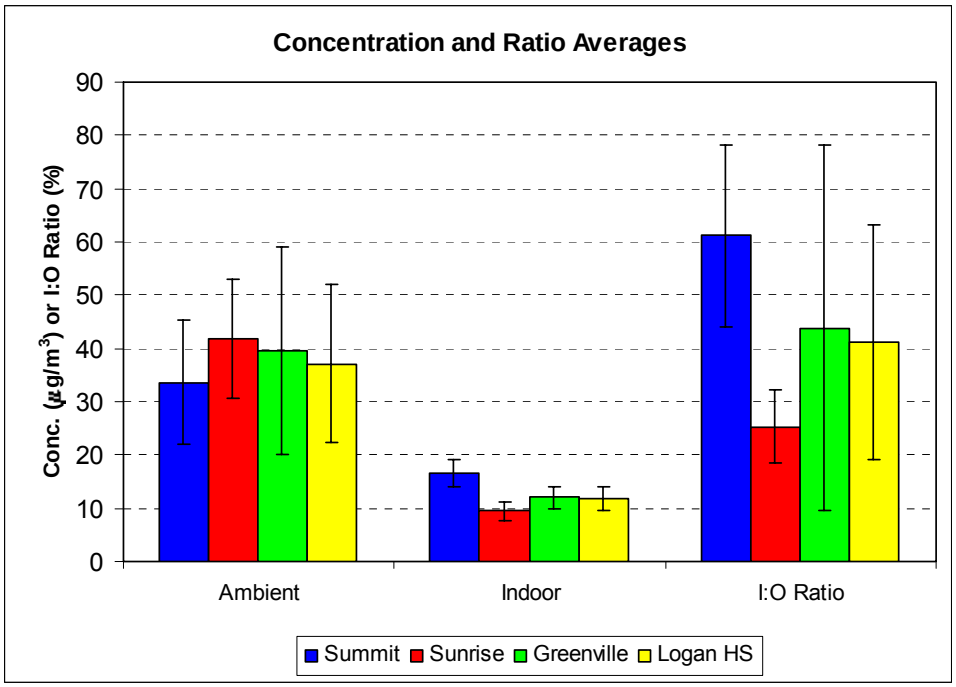

Figure 55. Average $PM_{2.5}$ levels and indoor:outdoor ratio by school.

It is believed that the mechanism used by the heating system in each school may affect the indoor $PM_{2.5}$ concentrations. Greenville Elementary, Sunrise Elementary, and Logan High School heat the buildings by passing air through a heater and blowing the heated air throughout the building (central heating). Summit Elementary uses steam heaters to heat the air in some of the rooms, producing less air circulation than the other schools. Circulation of the heated air provides a more uniform air temperature and mixes suspended particles more uniformly as well. As mentioned earlier, air temperature greatly affects the formation and volatilization of ammonium nitrate. The difference in heating mechanisms between Summit Elementary and the other three schools would have an affect on the total particle mass due to the volatilization of ammonium nitrate.

The chemical analyses of the particles collected on the filters through anion chromatography confirmed that nitrate dominates the outdoor particle composition (Figure 56). It also revealed that the average concentration of NO_3^- in the indoor air of

the three elementary schools was six times less than the outdoor concentrations, producing an average indoor:outdoor nitrate concentration ration of 17%. The indoor and outdoor nitrite (NO_2^-) levels were below the method detection limit. The particulate concentration of Cl^- was twice as high indoors as outdoors, which could be due to sources within the building. The SO_4^- concentrations were much closer than either the NO_3^- or the Cl^- with an average indoor:outdoor ratio of 85%. Cation chromatography was not performed because the complimentary cation for SO_4^- and NO_3^- is believed to be ammonium (NH_4^+). The differences in the indoor:outdoor particle composition ratios between elementary schools is found in Figure 57. Due to the dominance of ammonium nitrate in the particle mass, only the NO_3^- anion indoor:outdoor ratio was examined. The error bars represent the 95% confidence interval. The average indoor:outdoor NO_3^- ratios are not statistically different with the small number of data points collected, but there appears to be an higher concentration trend in data collected at Summit Elementary, the school that uses steam heaters to heat the building. More data collection at all sites is required to more completely quantify any difference in NO_3^- levels.

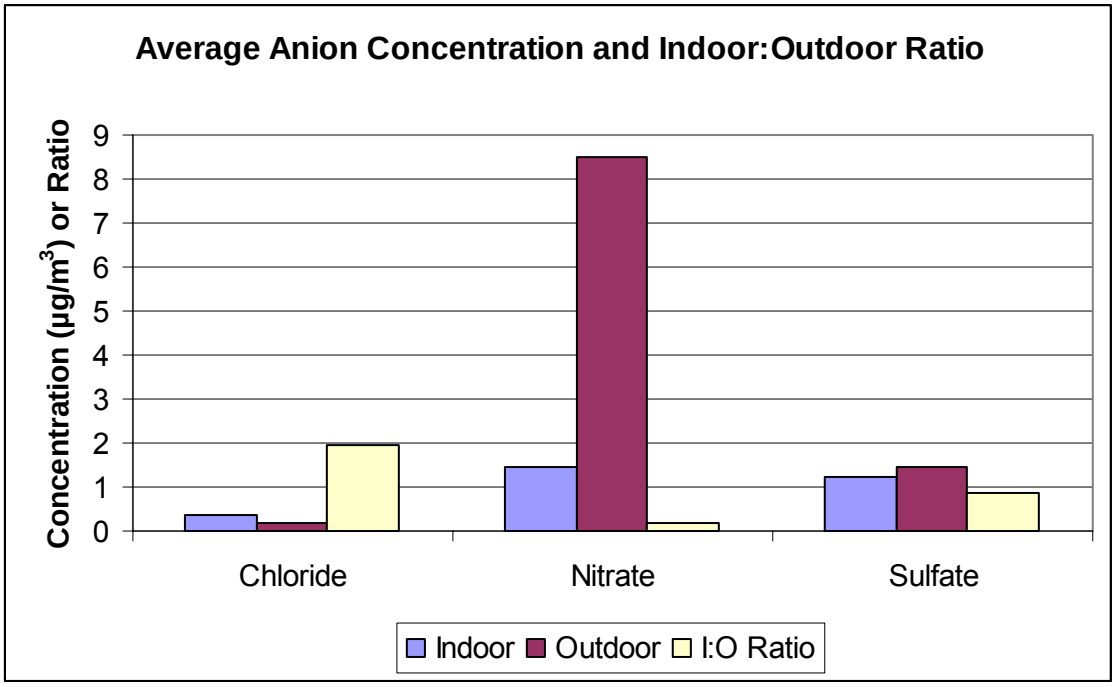

Figure 56. Anion concentrations in indoor and outdoor $PM_{2.5}$.

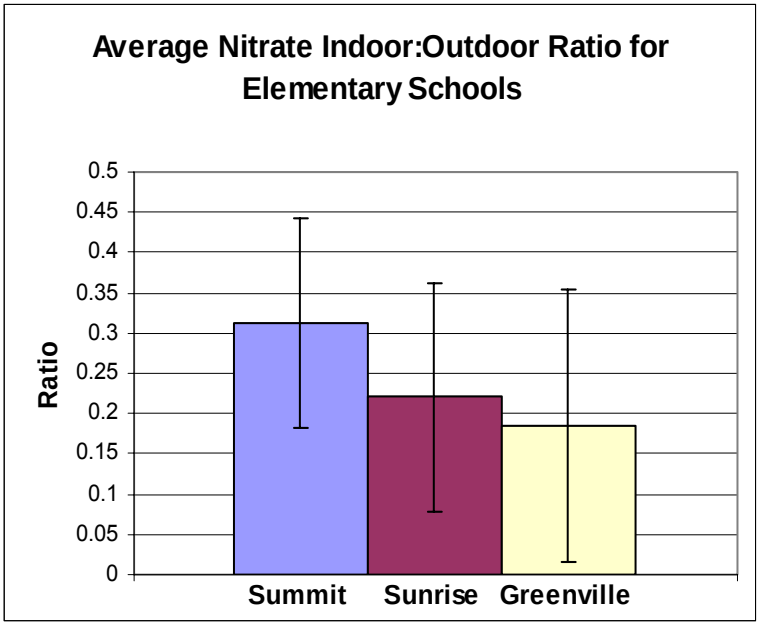

Figure 57. Average nitrate indoor:outdoor ratios for the Elementary Schools

CONCLUSIONS

Winter-time $PM_{2.5}$ concentrations above the national standard in Cache Valley have led area schools to keep children inside during recess and lunch time on "red" days as suggested by the Bear River Health Department. Indoor $PM_{2.5}$ concentrations versus ambient $PM_{2.5}$ were studied in four area schools and chemically analyzed in order to quantify indoor concentrations and particulate composition.

The average measured indoor $PM_{2.5}$ concentrations at the four schools was 12.5 $\mu g/m^3$, well below the 40 $\mu g/m^3$ level at which children start to be affected, even when ambient concentrations approach and exceed the national standard of 65 $\mu g/m^3$. Anion analysis of the collected particles confirmed that ammonium nitrate is the dominant chemical species in ambient $PM_{2.5}$, but the indoor NO_3^- concentrations are on average 17% of the outdoor concentrations. This difference in NO_3^- concentrations is likely due to ammonium nitrate volatilization as the temperature increases from ambient temperature to room temperature. The indoor $PM_{2.5}$ levels were, therefore, found "safe" in all four schools at the ambient concentrations measured. Keeping the children inside during high pollution days was in their best interest and protected them from exposure to unhealthy levels of particulate matter.

WINTERTIME VERTICAL OZONE DISTRIBUTIONS

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INTRODUCTION

Research discussed in previous sections showed that the main contributor to the $PM_{2.5}$ in the Cache Valley was photochemically derived ammonium-nitrate (NH_4NO_3). Along with the precursor compounds of ammonia (NH_3) and oxides of nitrogen (NO_x), the formation of ammonium-nitrate is fueled by ozone and sunlight. Although considerably more reactions are involved, Equations 1-4 show the basic NH_4NO_3 formation mechanisms.

$$O_3 + sunlight \rightarrow O^1D + O_2 \qquad (Eq\ 1)$$

$$O^1D + H_2O \rightarrow 2OH \qquad (Eq\ 2)$$

$$OH + NO_2 \rightarrow HNO_3 \qquad (Eq\ 3)$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \qquad (Eq\ 4)$$

As shown above ozone (O_3) reacts with available incoming solar radiation (insolation) of about 310 nm, or less, to form O singlet D (O^1D), an excited oxygen atom, as well as diatomic oxygen (O_2). The O^1D then reacts with water vapor to form two hydroxyl radicals. Hydroxyl radicals are highly reactive and readily combine with any available nitrogen dioxide (NO_2), produced from car emissions and other combustion sources, to give nitric acid (HNO_3), which when combined with gas-phase ammonia forms NH_4NO_3. Furthermore, ozone is known to accelerate the oxidation of hydrocarbons and other pollutants in quantities as low as 20 ppb which can complicate and accelerate the above reactions (Woods Hole, 2006).

Ozone is also the product of a complex series of reactions strongly dependent on available sunlight (≤420 nm) as summarized in Equation 5:

$$NO_2 + NMHCs + sunlight \rightarrow O_3 + products \qquad (Eq\ 5)$$

where NMHCs represents non-methane hydrocarbons. Typically these reactions are expected to be dominant in the summertime when there is plenty of available sunlight. However, Cache Valley's global location (41.8°N) and frequent wintertime clouds, storms, and fog episodes, were not thought to allow enough insolation to produce enough ozone or to adequately drive Equations 1 and 5.

Uncertainty in the local wintertime ozone levels led investigators (Dr. Martin) to establish an ozone monitoring site in downtown Logan, situated in the heart of Cache Valley, from February to April of 2004. Previously, ozone had only been monitored in Logan for regulatory purposes by the Utah Division of Air Quality (UDAQ) during the summer months; however, since the brief study of Martin, the UDAQ has established year-round ozone monitoring at the specified location. As shown in Figure 58, wintertime ozone concentrations peaked as high as 70 ppb, with average peak values

around 45-55 ppb. The overall daily averages were on the order of 25-35 ppb. These unexpectedly high wintertime ozone values indicate sufficient oxidation potential to initiate the previously discussed reaction pathways toward ammonium nitrate formation (Refer to Equations 1-5).

The source of the observed high concentrations of O_3 was still uncertain, particularly in regards to the lack of available insolation. However, somewhat in support of these high wintertime values Lefohn *et al.* (2001) reported finding hourly average ozone concentrations greater than or equal to 50 and 60 ppb during photochemically quiescent months in the winter and spring at several rural sites across southern Canada, the northern United States (Wyoming), and northern Europe.

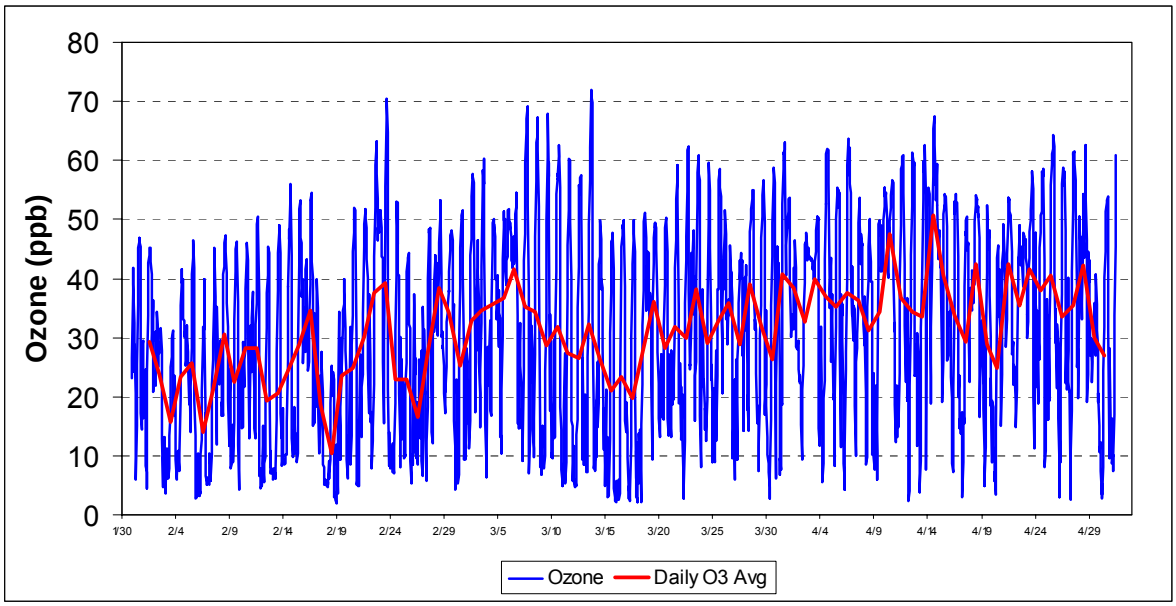


Figure 58. Logan O_3 February-April 2004.

For the Cache Valley situation, it was speculated that free tropospheric ozone could be the source of the elevated ground level ozone, assuming the possibility or likelihood of sufficient downward mixing. As such, an experiment was designed to measure the local wintertime vertical ozone profile. If elevated concentrations were observed above the ground level or the inversion heights, the upper level ozone may be the source for the unexpectedly high concentrations recorded at the Logan station.

METHODOLOGY

In order to measure the vertical ozone concentrations a small airplane was outfitted with an ozone monitor, a temperature monitor, a GPS system, and two flights were conducted. The first flight was in the mid-afternoon of February 9, 2006 (13:41-15:32). The second flight was in the early morning, just after sunrise, on February 11, 2006 (7:02-8:59). A four meter Teflon tube with an outer diameter of ¼" was attached to

the wing strut of a Cessna 182 airplane. The tube ran to the inside of the plane and was attached to a ThermoEnvironmental Model 49C UV Photometric O_3 Analyzer. Before the initial flight, the ozone monitor was calibrated using a ThermoEnvironmental Model 49C Primary Standard O_3 Calibrator. The data were averaged over one minute intervals and corrected for system sampling and instrument response time lags (approximately one minute). A HOBO temperature sensor was attached to the opposite strut and programmed for 15 second averaging periods. A Garmin Etrex Vista handheld GPS was used to track aircraft position and altitude. The flights were on a north-south transect along the length of the valley at above sea level elevations of around 1460 m, 1600 m, 1950 m, and 2770 m, or above the valley floor elevations of approximately 90 m, 300 m, 600 m, 1400 m. A sample flight path (February 9) can be seen in Figure 59. The flight path for the second profile (February 11) was similar.

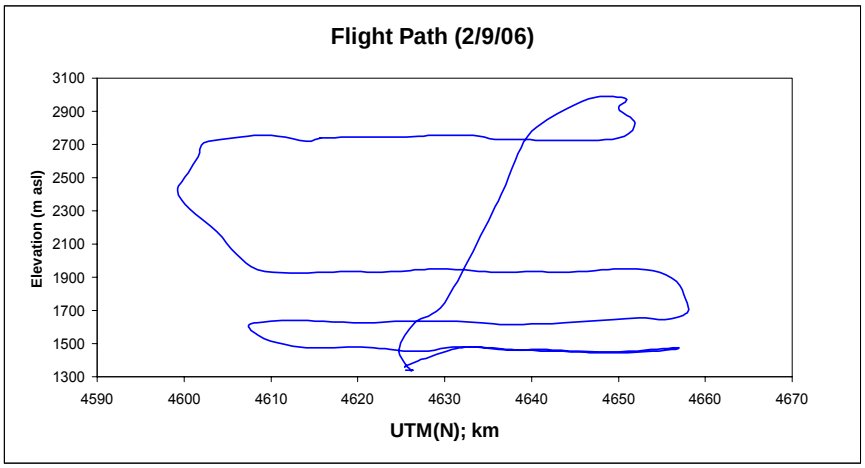


Figure 59. Flight path for February 9, 2006.

RESULTS

During the first flight ground level ozone concnetrations measured just before takeoff and after landing, were found to average approximately 35 ppb. At the UDAQ Logan station, approximately 5.6 km from the airport location, during the same time period ground level ozone was measured to be approximately 34-48 ppb (UDAQ, 2006). The ozone concentrations along the flight path are shown in Figure 59. The different elevation transects above the valley floor are shown in different colors (see legend on Figure 59). For most of the elevations flown, ozone concentrations were moderately consistent varying between 40-50 ppb. However, at the lower two transects, 90 m and 300 m above ground level, the ozone concentrations displayed a noticeable decrease when flying over the mid-to-south end of the valley, the most densely populated area of the valley. Additionally, it should be noted that there was a 1.4 – 1.9 m/s wind blowing out of the Northwest. The investigators theorize that the reason the "Logan Dip," as it was referred to, was not seen at the third and fourth transects (600 m – 1400 m) is because these final two transects were above the inversion height. Figure 60 shows a

photograph taken from an elevation of approximately 1900 m (asl) clearly showing the inversion layer.

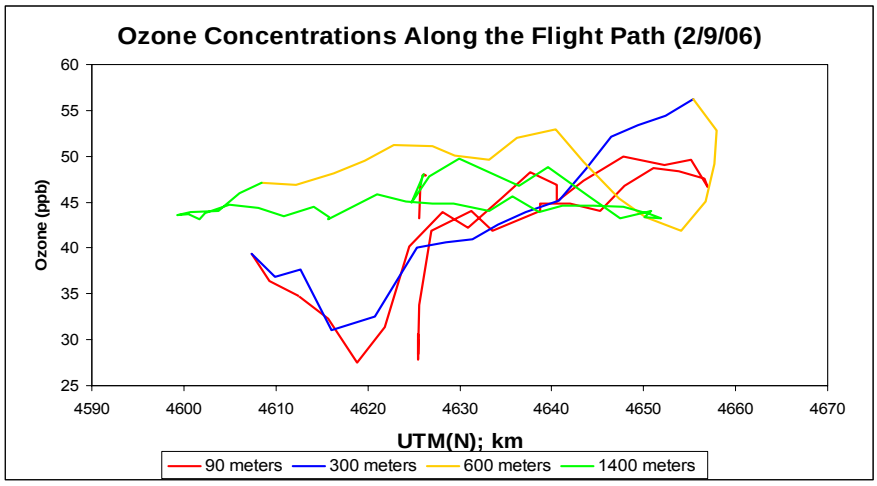


Figure 59. Ozone concentrations along February 9, 2006 flight path (elevation transects are above ground level).

Figure 60. Photograph of inversion above Cache Valley, Utah taken 2/9/06 at 1900 m (asl).

The valley-wide average vertical ozone profile from the same day is shown in Figure 61. The ozone concentrations were low at ground level and rose to values approaching 50 ppb, then began to decrease at above sea level elevations of around 2000 m. The 95% confidence intervals have a higher degree of variability at lower elevations. This coincides with the variability owing to the "Logan Dip" seen in Figure 59.

However, above the inversion layer the 95% confidence intervals are small because the ozone was essentially the same horizontally (north-to-south) through the measured troposphere.

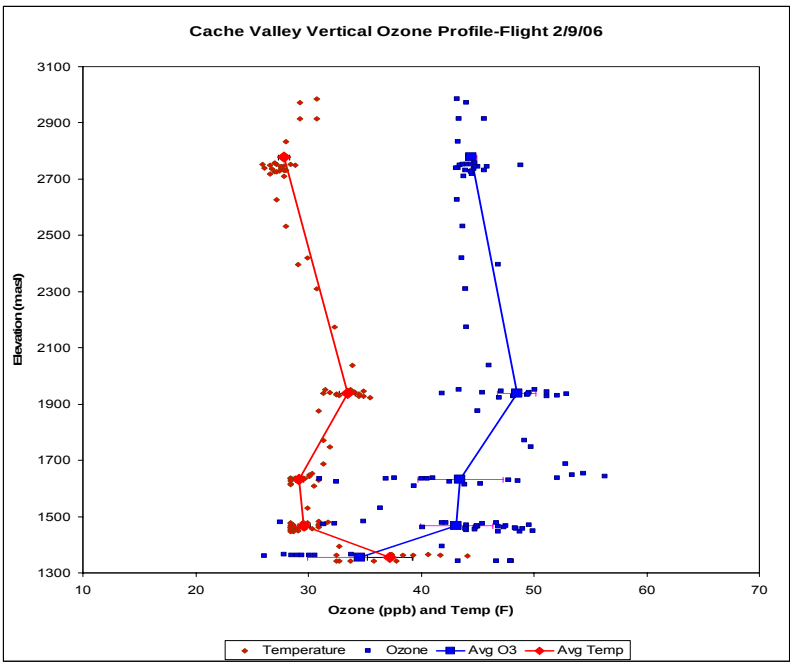


Figure 61. Vertical temperature and ozone profile February 9 flight (error bars represent the 95% confidence interval).

Also shown in Figure 61 is the vertical temperature profile for the February 9th flight. As described by Cooper and Alley (2002), an inversion is when temperature increases with altitude as opposed to the typical case of temperature decreasing vertically. A very pronounced inversion can be seen clearly delineated at approximately 650 m above ground level (2000 m asl). Most of the locally emitted reactive pollutants remain trapped under the inversion layer and are more concentrated at the south end of the valley due to population density and wind direction. This is also evidenced by the "Logan Dip" in Figure 59.

The second flight in the early morning of February 11, 2006 found that ground level ozone was between 16-31 ppb. UDAQ reported that on that morning the Logan station ground level ozone was measured to be approximately 19-33 ppb (UDAQ, 2006). The ozone concentrations along the flight path are shown in Figure 62. As with the previous flight (Figure 59) the different elevation transects above the valley floor are shown in different colors (Figure 62). On the morning of the 11th, ozone concentrations were more consistent in regards to north-south variability and generally increased with elevation.

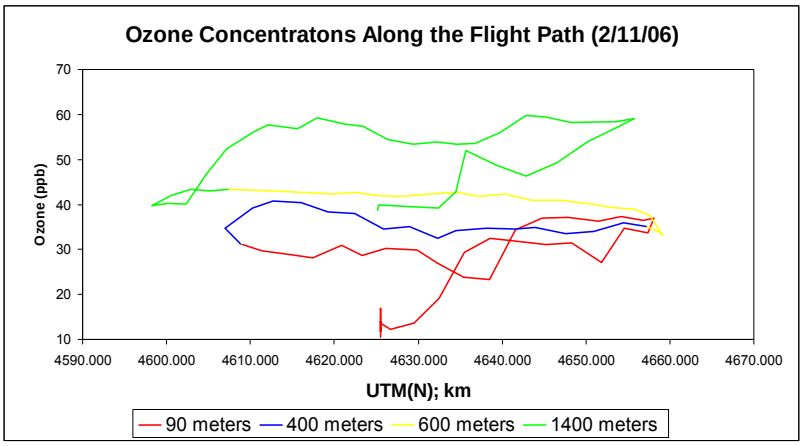


Figure 62. Ozone concentrations along February 11, 2006 flight path (elevation transects are above ground level).

Figure 63 shows the vertical temperature and ozone profiles for the February 11th flight. As elevation increased, there was a gradual increase in ozone up to approximately the same background concentration as observed on the February 9th afternoon flight. Once again the observed ground level ozone showed the highest degree of variability, which is likely due to different concentrations observed between the start (take-off) and ending (landing) of the flight period.

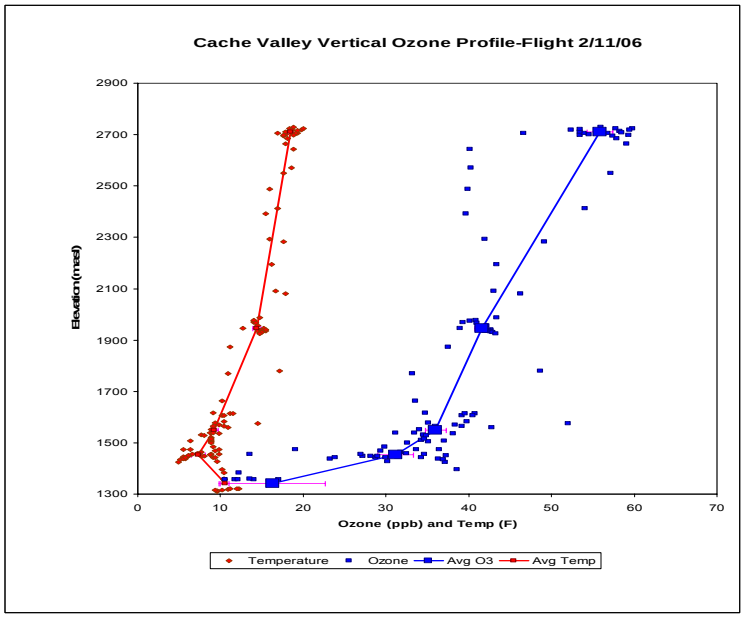


Figure 63. Vertical temperature and ozone profile February 9 flight.

This flight started before sunrise, at which point ground level ozone had had sufficient time overnight to titrate out by reacting with hydrocarbons and oxides of nitrogen. Upon landing the sun had risen and ozone formation chemistry had already

begun (more insolation). The temperature profile (Figure 63) showed that there was a moderate, continuous inversion from ground level to the highest elevation.

CONCLUSIONS

Upon analysis of the data it was concluded that the wintertime high levels of ozone in Utah's Cache Valley could indeed be a result of downward mixing from ozone aloft. The upper-level available ozone is likely being utilized at ground level, as well as produced, through the previously mentioned photochemical reactions to form particulate-phase ammonium nitrate.

Figure 64 directly compares the ozone concentrations from both flights. The ground level ozone was low in the morning hours compared to the afternoon flight due to reactions previously discussed.

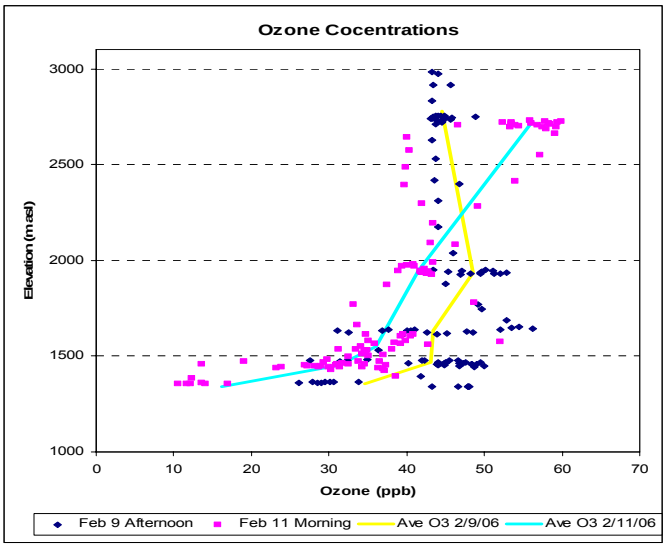
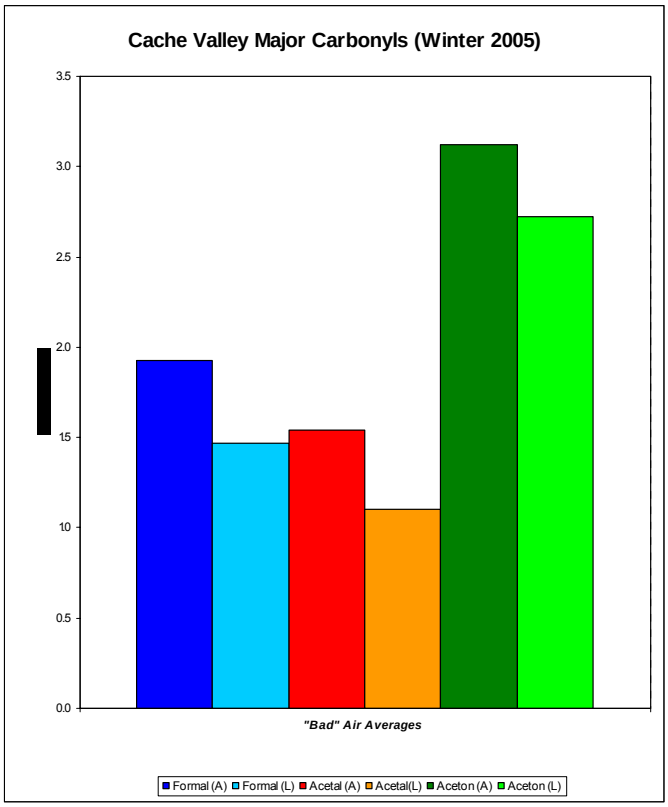
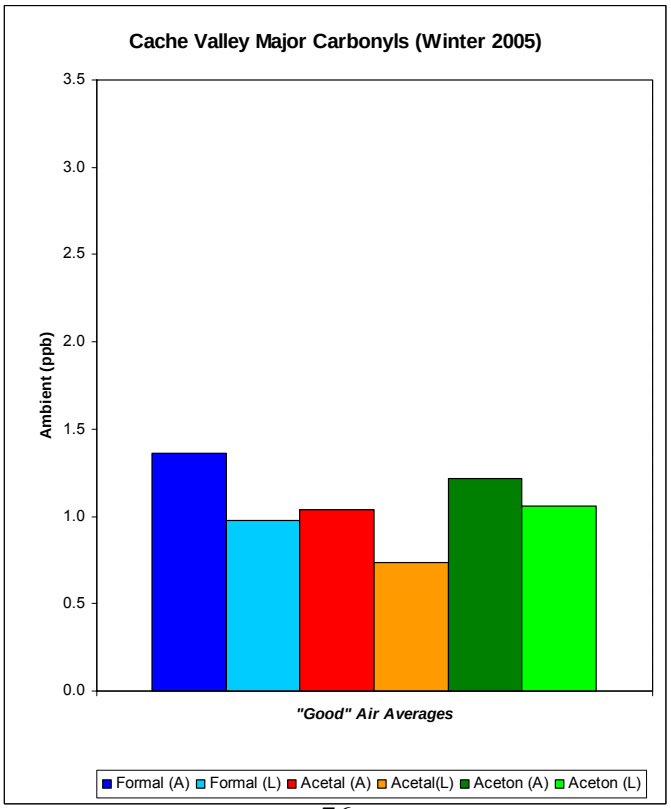


Figure 64. Ozone Concentration-both flights.

In the afternoon, a very pronounced dip in ozone concentrations over Logan served as evidence that the ozone is reacting with pollutants within the inversion boundary. The ozone concentrations were similar (45-55 ppb) above the inversion and generally increased with elevation. Although this study gives strong indication that free tropospheric ozone may supply sufficient concentrations to initiate photochemical reactions in Northern Utah's Cache Valley, it is recommended that additional vertical ozone profiles be measured to determine if these results are typical throughout the winter period. Airplane transects are expensive and time consuming. It is suggested that other methods, such as radio sondes or tether sondes, be used for further analysis.

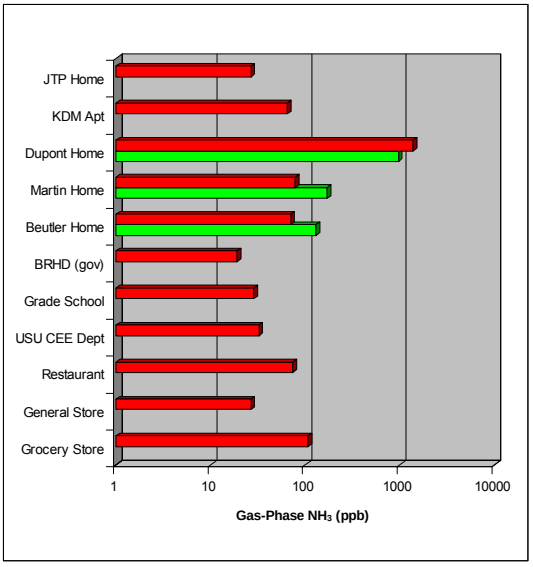
VOCs

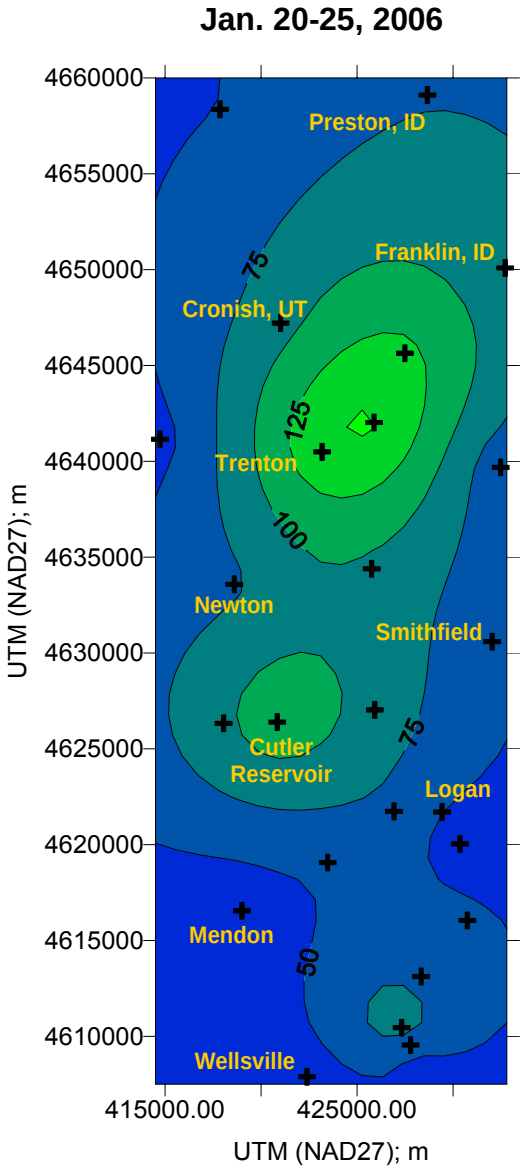

Cache Valley Major Carbonyls (Winter 2005)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
"Bad" Air Averages
Formal (A)
Formal (L)
Acetal (A)
Acetal(L)
Aceton (A)
Aceton (L)


Cache Valley Major Carbonyls (Winter 2005)
Ambient (ppb)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
"Good" Air Averages
Formal (A)
Formal (L)
Acetal (A)
Acetal(L)
Aceton (A)
Aceton (L)

NEW RESEARCH

Indoor NH3,
Valley-wide NH3





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